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PREVENTION AND EXTINGUISHMENT OF FIRES INVOLVING
HYPERGOLIC PROPELLANTS

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I INTRODUCTION

In an earlier assignment (November-December 1967) the Bureau of Mines investigated the likely effectiveness of a proposed Halon 1301 system for inerting the atmosphere of the Spacecraft-LM Adapter (SLA). The conclusions reached after a 30-day experimental program were that Halon 1301 could provide some protection as an inerting agent for spills of A-50, and that it could serve well to extinguish secondary fires of many flight vehicle combustibles; however, it was disappointingly ineffective in combatting an established fire of A-50, and led to toxic combustion products and to visibility-limiting smoke.

It was recommended that the Halon 1301 installation be pursued but that further investigation be made - first, of the extent of protection afforded by Halon 1301 alone; and second, of ways in which water or CO₂ could profitably be used along with Halon 1301 to give better protection.

A complete statement of Tasks A-J of the present study is given in Appendix I. The experimental results are presented below and correlated where possible with the earlier work.

II RESULTS AND DISCUSSION

Task A - Water Dilution Ratios

1. Vapor/Air Ignitions

Flammable water-soluble materials such as A-50 can be made nonflammable in air by dilution with water; the amount of water required depends primarily on the ambient temperature (12). Thus at one atmosphere pressure an A-50/water mixture must contain at least 37 weight percent water to produce nonflammable vapors in a Cleveland Open Cup apparatus (1) at 77° F (25° C), and 48 weight percent water in a Tag Closed Cup (2) under the same conditions (figure 1). In practice, these values depend on the actual composition of the A-50*. The amount of water required to produce nonflammable mixtures decreases as the UDMH content decreases; this situation prevails when A-50 evaporates in an open container or a pool.

Unfortunately, heat is evolved when water is added to A-50 so that the liquid temperature increases above that of the surroundings. For this reason, more water is needed initially to produce a nonflammable mixture (because of the elevated liquid temperature) than indicated by the data in figure 1. For example, figure 2 indicates that the water requirements are increased to about 65 weight percent when water is added to A-50 in an insulated open cup, as the liquid temperature increases from 75° (24° C) to 145° F (63° C) (note that the flash point data for this sample differ somewhat from those given in figure 1 but that the general conclusions are

*The sample used here contained 52.9 weight percent hydrazine and 46.9 weight percent UDMH (67.5 mole percent hydrazine; 32 mole percent UDMH).

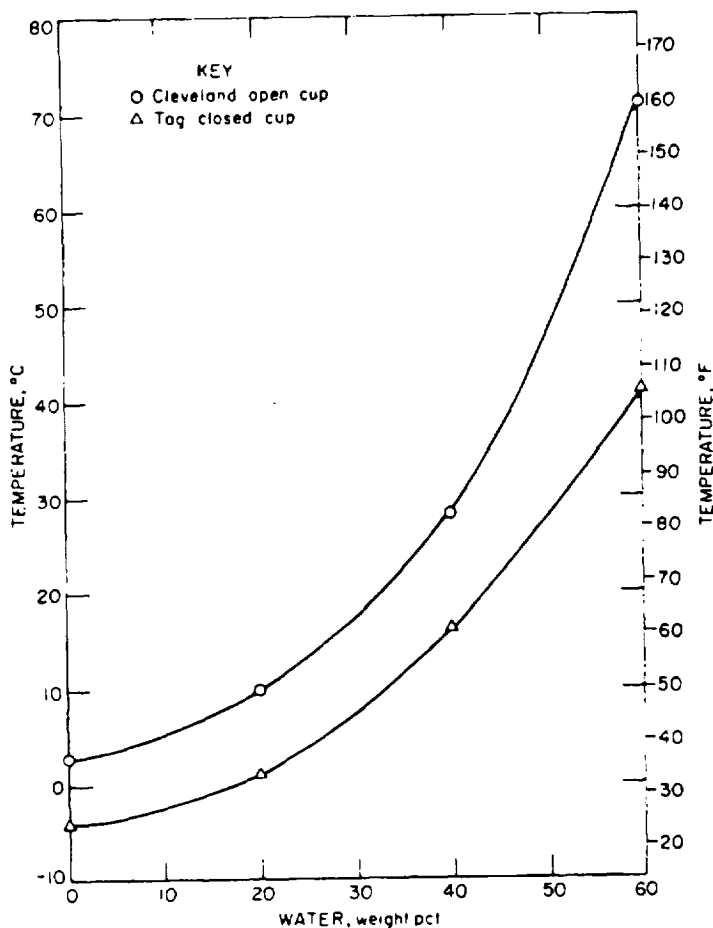


FIGURE 1. - Flash Points of A-50/Water Mixtures at Atmospheric Pressure.

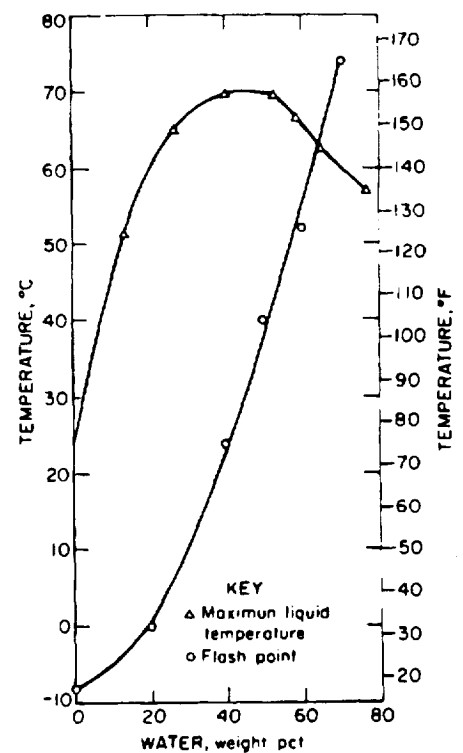


FIGURE 2. - Maximum Temperatures Attained by Mixing A-50 and Water at 24° C Superimposed on the Open Cup Flash Point Diagram of A-50/Water at Atmospheric Pressure.

still valid - that is, the water requirements are increased appreciably if an ignition source is present when water dilution occurs).

The flash point and water dilution data for monomethylhydrazine (MMH) are given in figures 3 and 4. Again, water requirements are increased because of the heat generated when dilution occurs. Here the water requirements go up from about 12 to 50 weight percent in the open cup at an initial temperature of about 77° F (25° C). Even more water would be needed in each case to inert the vapor above a liquid in a closed space, although in the first case the picture is clouded somewhat as the composition of the "air" above the liquid changes because of the reaction between A-50 and oxygen.

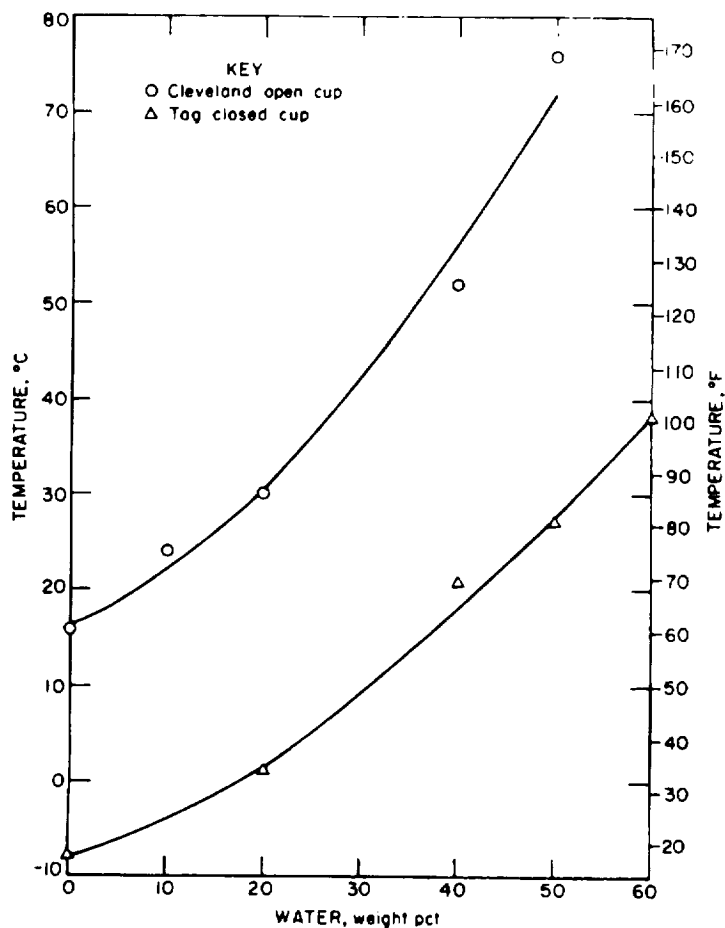


FIGURE 3. - Flash Points of MMH/Water Mixtures at Atmospheric Pressure.

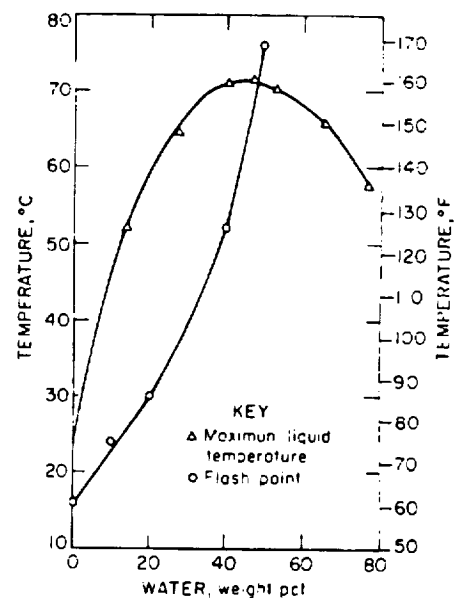


FIGURE 4. - Maximum Temperatures Attained by MMH/Water Mixtures at 25° C Superimposed on the Open Cup Flash Point Diagram of MMH at Atmospheric Pressure.

The vapors above a series of liquid UDMH-hydrazine-water mixtures were found to be flammable at ambient temperatures. Further, when ignited they continued to burn until the water content of the residual liquid was so high that combustion could no longer be supported. The five mixtures labeled 1, 2 ... 5 in figure 5 burned until the mixture compositions became those labeled 1', 2', ... 5' and the flame above the liquid pool went out; the solid symbols represent flammable mixtures and the open symbols, except for 9, 10 and 11 which are discussed under Task E, non-flammable mixtures. Border-line compositions between the flammable and

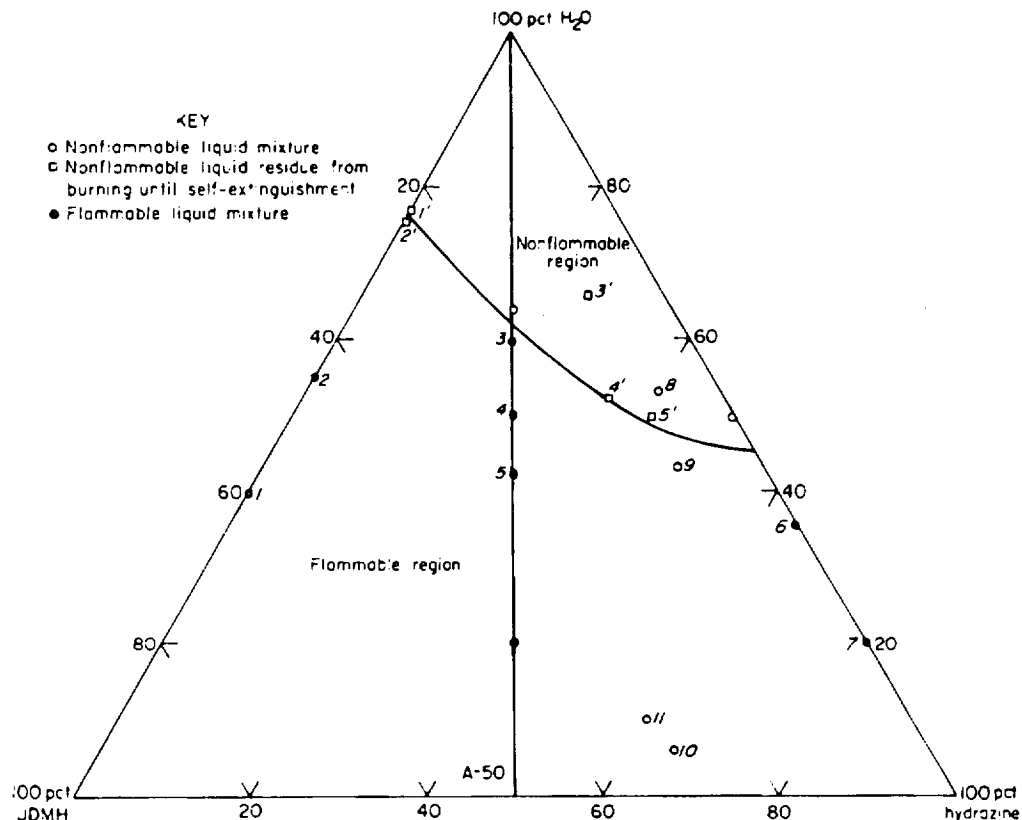


FIGURE 5. - Combustion Properties of UDMH-Hydrazine-Water Mixtures in Air at Ambient Temperatures.

nonflammable regions occur at about 75 weight percent water with UDMH/water mixtures, 65 weight percent water with the A-50/water mixtures, and about 45-50 weight percent water, with the hydrazine/water mixtures. Thus we can consider the use of a 2:1 water dilution ratio (i.e. 2 lbs of water per lb of A-50) adequate to prevent the formation of a flammable mixture following an A-50 spill.

2. Prevention of Hypergolic Ignition

When both fuel (A-50 or MMH) and oxidizer (N₂O₄) spill or leak into the same area, one or the other, or both, must be diluted with water to prevent a hypergolic reaction. Three situations are considered here: (1) neat oxidizer contacts water-diluted fuel, (2) neat fuel contacts water-diluted oxidizer, and (3) water-diluted fuel contacts water-diluted

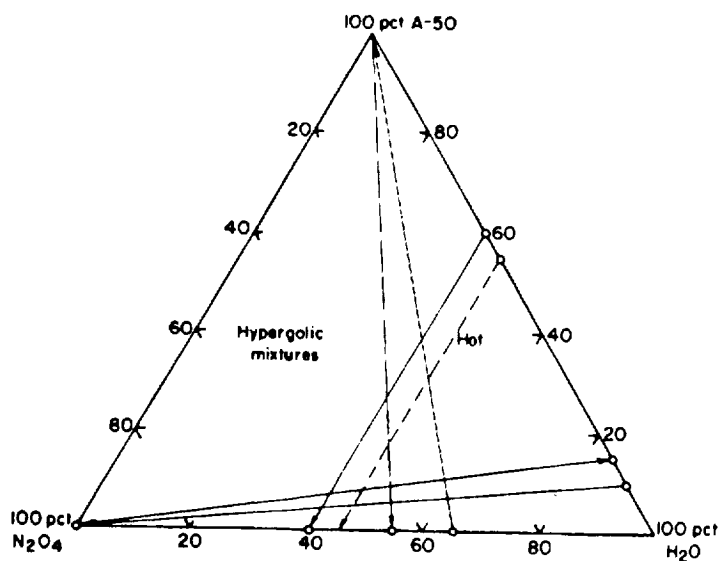


FIGURE 6. - Critical Hypergolic A-50/Water-N₂O₄ Mixtures at Ambient Temperatures.

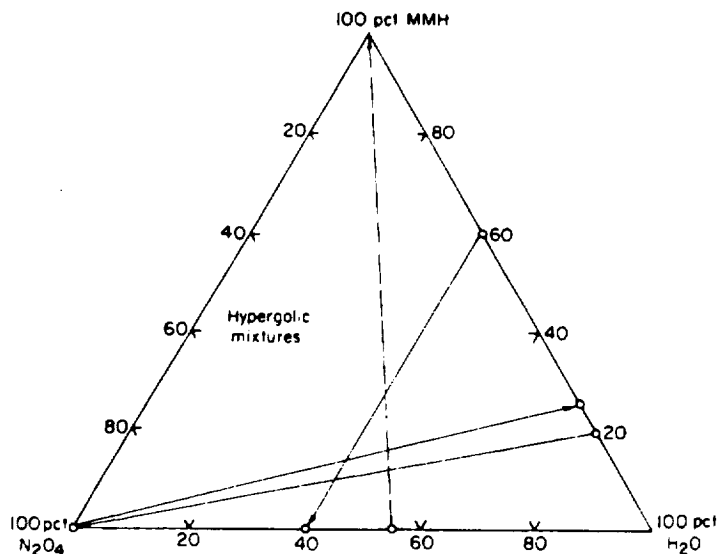


FIGURE 7. - Critical Hypergolic MMH/Water-N₂O₄ Mixtures at Ambient Temperatures.

oxidizer. A series of experiments was conducted with A-50 and MMH to determine the critical amounts of water needed to prevent a violent reaction. If only one stream is diluted with water, as much as approximately 10 times the fuel weight (of water) is required with A-50 and 5 times the fuel weight with MMH to produce non-hypergolic mixtures. If ignition occurs, a 2:1 dilution with water is sufficient to extinguish the fuel fire in air. A summary of the data obtained near the critical region is presented in Appendix II and the critical experiments are summarized in figures 6 and 7. In each case, combinations to the left of the directed straight lines within the triangular areas represent hypergolic mixtures; the arrows give the directions in which liquids were poured. Thus for example, the addition of neat N₂O₄ to A-50/H₂O mixtures containing less than 85 weight percent H₂O produces a hypergolic reaction (figure 6); similarly, the addition of neat N₂O₄ to MMH/H₂O mixtures containing less than 75 weight percent H₂O

produces the same result. If water is added to both the fuel and oxidizer, hypergolic ignition can be circumvented by the dilution of each material with equal weights of water. However, a temperature rise will occur even if ignition is not obtained, as heat is released when fuel and oxidizer are combined. Temperatures in excess of 180° F have been obtained without an ignition (Appendix II).

The broken line labeled "Hot" (figure 6) was obtained by pouring the A-50/water mixture while it was still hot from the heat of solution into an equally diluted but cool N_2O_4 /water mixture. While this widens the hypergolic range somewhat, again equal dilution with water would be adequate to prevent ignition.

3. Recommendations Relative to Task A

In the event of a minor leak (less than a pound, say) of A-50 our results show that the system can be inerted with very modest additions of water. However, this implies that the water must find its way to the same out-of-the-way location as the liquid A-50. It does not suffice to add 2 lbs of water spray to the SLA when the one lb of fuel has collected in some small pool. Furthermore, during the early stages of the slow addition of water to fuel (as by the settling of a fog) the system's temperature may be farther above flash point than without the water (see figures 2 and 4).

These considerations imply that a small hand-directed water stream may be more useful than an undirected spray or fog; also that any "deluge" must be truly overpowering to fulfill its intended purpose.

Task B - Evaporation

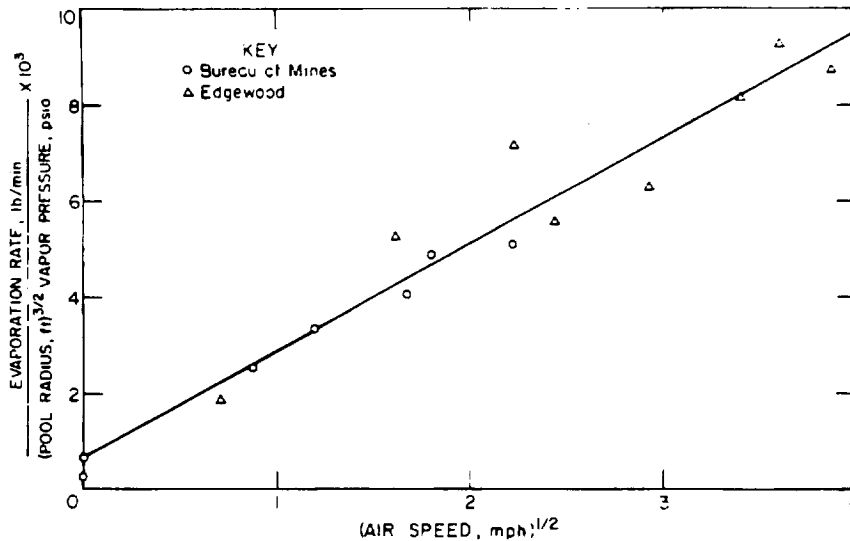


FIGURE 8. - Evaporation Rate of A-50 from Shallow Pools.

This subject has received so much attention that the main problem is to choose discriminatingly from available information and to avoid undertakings aimed at producing new basic data. It seemed immediately that a vaporizing pool would be the most interesting spill situation (as compared with drips, trickles and sprays) in the sense of providing unusual hazards related to the propellant's volatility, vapor density, and flammability. It was also learned at the outset that Edgewood Arsenal

had been studying the evaporation of A-50 and N_2O_4 pools from 4-ft square trays in natural winds. Their completed study of N_2O_4 was available as a Technical Memorandum* and their data on A-50 evaporation were made available to us in undigested form (9).

1. Evaporation Rates

There are long-established empirical equations (6) by which the rate of evaporation from a liquid surface, $\frac{dw}{dt}$, is said to depend on the vapor pressure of the liquid, p_s , the square root of the wind speed, V , and the $3/2$ power of pool radius r . Thus

$$\frac{dw}{dt}, \text{ lbs/min} = k (p_s)^{1/2} (V)^{3/2} (r) \quad (1)$$

or

$$\frac{dw}{dt} / p_s \cdot r^{3/2} = k V^{1/2} \quad (2)$$

but since the evaporation rate is not zero at zero air speed,

$$\frac{dw}{dt} / p_s \cdot r^{3/2} = k_0 + k \cdot V^{1/2} \quad (3)$$

*Appendix III includes a review of Edgewood Arsenal TM 211-1 of August 1966.

These equations were tested with eight Edgewood Arsenal measurements at (natural) wind speeds up to 15 mph and with six Bureau tests using fan-driven air flows in the 0-5 mph range. Liquid temperatures in the Edgewood tests ranged from 40 to 109°F giving vapor pressures, p_s , from 1.1 to 5.6 psia (13). The effective pool radius, r , varied about four-fold from the 14-in. diameter aluminum tray used here to the 4-ft square tray at Edgewood. Considering these variations, the correlation coefficient, 0.97, of the data in figure 8 seems to be very good.

Monomethylhydrazine vaporizes at a somewhat slower rate than A-50 under forced ventilation conditions. The following rate data were obtained at 72 to 77° F in a 14-in. diameter tray at 175 and 300 ft/min air speed respectively (1.9 and 3.4 mile/hr): 4.8×10^{-3} and 6.8×10^{-3} lb/ft² min; the vaporization rate was found to be about 0.001 lb/ft²-min in a quiescent atmosphere. The trend is the same as that found for A-50 (figure 8).

For completeness, a discussion of the evaporation of nitrogen tetroxide is given in Appendix III. While not listed as a part of our study, the data obtained at Edgewood Arsenal were used to design the experiments conducted here.

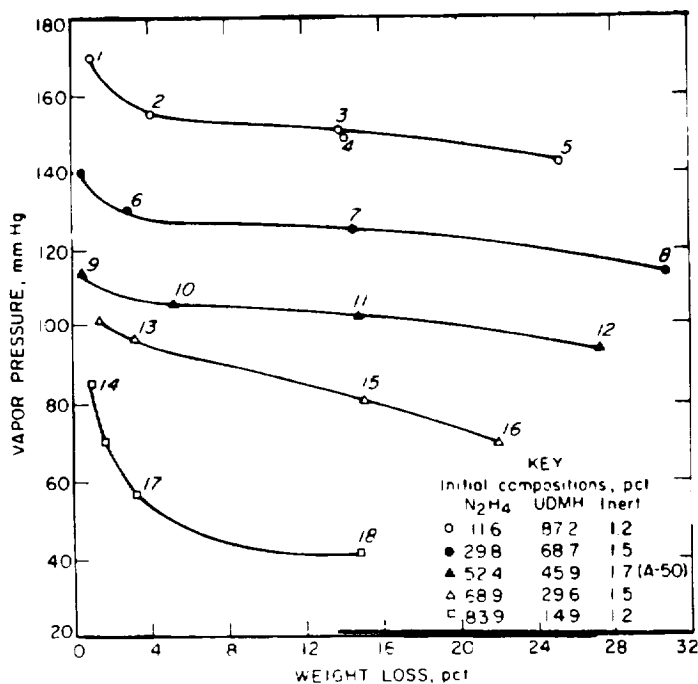


FIGURE 9. - Vapor Pressures of Various Hydrazine-UDMH Mixtures as a Function of the Evaporative Weight Loss at 77° F (25° C).

2. Vapor Pressure

As noted above, the evaporation rate of a liquid depends in part on its vapor pressure. Accordingly, vapor pressure measurements were made on A-50 and on synthetic mixtures of hydrazine and UDMH with an isoteniscope at 77° F (25° C) and at 104° F (40° C). The liquid sample was first boiled at reduced pressures to remove dissolved gases. However, this also affected the liquid composition and tended to lower the vapor pressure of the residual liquid. For example, figure 9 gives the measured vapor pressures for a series of liquid mixtures after varying amounts of liquid were lost by vaporization at 77° F (25° C). An analysis of the residual liquid was used

to determine the composition of the liquid and of the vapors above the liquid. These data are plotted on the distillation or vapor-liquid equilibrium curves given in figure 10; the curves were obtained from published 104-212° F (40°-100° C) hydrazine-UDMH distillation data (8). The numbers next to the plotted points (circles) give the sequence in which determinations were made. Note in particular that the first few determinations did not lie along the liquidus curve as the corresponding vapor pressure was too high because of the presence of dissolved gases (hydrogen, air, methane, ammonia, methylamine and dimethylamine were found by use of a gas chromatograph) in a sample that had been stored for a period of time. After these were removed, the liquid and vapor compositions were in agreement with the extrapolated data of reference 8 (figure 10). Similar results have been obtained at 104° F (40° C); these data are presented in figure 11. They were used to construct the vapor-liquid equilibrium curves of figure 12.

The gas saturation method (11) was used to determine the composition of the vapors above various A-50/water mixtures at 25° C. Dry helium was used as the carrier gas. Three glacial acetic acid scrubbers were used to absorb the A-50 vapors; the hydrazine and UDMH contents of the glacial acetic acid were determined by non-aqueous titration with

perchloric acid, and the water vapor concentration in the vapor phase was determined by difference from the weight lost by the original A-50/water mixture. The data obtained by this procedure are presented in figure 13. These show the non-ideal behavior of A-50/water mixtures at 77° F (25° C); note in particular that the total vapor pressure above the liquid is considerably lower than that predicted by Raoult's law (Ideal Solution).

3. Vapor Concentration Above a Pool

Two problems are of interest here. The first involves the spillage of liquid A-50 in an enclosed

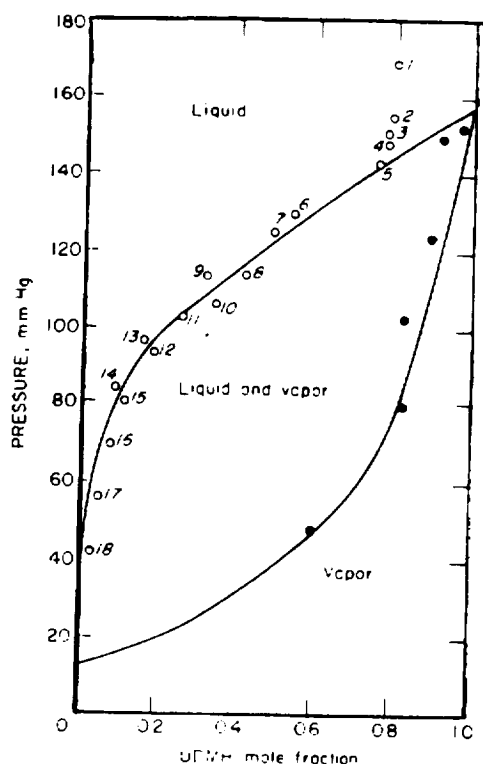


FIGURE 10. - Vapor-Liquid Equilibrium, N_2H_4 /UDMH Solutions, 77° F (25° C).

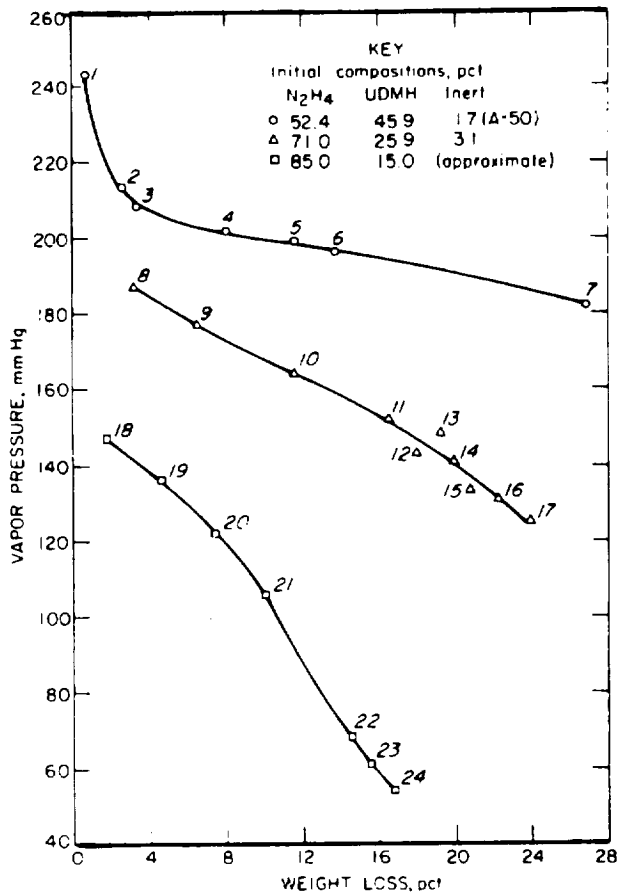


FIGURE 11. - Vapor Pressure of Various Hydrazine-UDMH Mixtures as a Function of the Evaporative Weight Loss at 104° F (40° C).

area, and the second, spillage in the open. In the first case, in the absence of forced ventilation and convection currents (diffusion limited) the liquid will vaporize slowly and the vapors will ultimately fill the space above the liquid. If sufficient liquid is available, the vapor concentration will approach the equilibrium value corresponding to the liquid pool temperature (assuming the air space above the liquid is at the same or at a higher temperature). Thus, if a large amount of liquid is spilled at 77° F (25° C), the UDMH vapor concentration above the pool approaches 13.5 volume percent and the hydrazine vapor concentration approaches 1.4 volume percent (cf figure 10). However, if a small amount of liquid is spilled, the initial vapor composition above the liquid will be about 13.5 volume percent UDMH and 1.4 volume percent hydrazine, but as this vapor diffuses upwards the vapor concentration will decrease and the ratio of hydrazine to UDMH will increase. In any event, the final composition will depend on the quantity of liquid spilled and the volume of the air space into which the vapor diffuses.

The rate at which vapor diffuses into the air space above a liquid pool in a spill situation in which liquid occupies the entire cross section of an enclosure depends on the vapor pressure (and therefore on the liquid temperature), on the height of the enclosure, and on the vapor concentration at the top of the enclosure. In the limiting case, the diffusion rate into

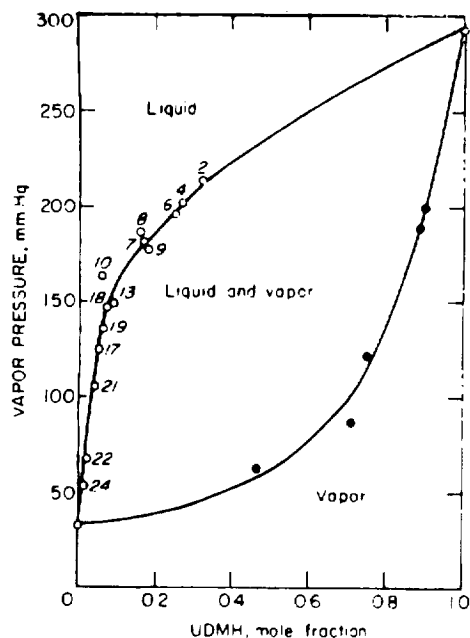


FIGURE 12. - Vapor-Liquid Equilibrium, N_2H_4 /UDMH Solutions, $104^\circ F$ ($40^\circ C$).

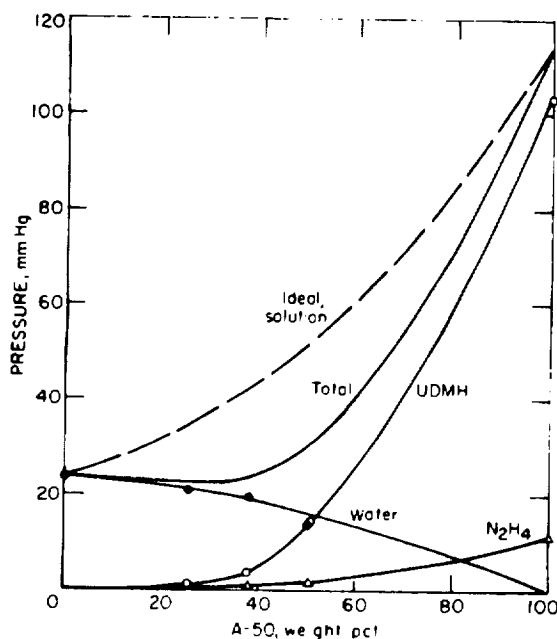


FIGURE 13. - Partial Pressures at Water, UDMH, and Hydrazine in the Vapor Phase Above A-50/Water Mixtures at $77^\circ F$ ($25^\circ C$) and Atmospheric Pressure.

still uncontaminated air is given by the zero air speed value in figure 8, for an enclosure of negligible height. Under equilibrium conditions the concentration at any level, z , in an enclosure from which vapor is removed at height, h , is found by solving the diffusion equation (7):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} = 0 \quad (4)$$

This gives for the concentration at any level:

$$c = c_e \left(1 - \frac{z}{h}\right) \quad (5)$$

where c_e is the equilibrium value determined solely by the vapor pressure of the liquid. In practice, there may be convection currents so that the steady-state concentration will be less than the calculated value at any height.

When equilibrium has not been established, the diffusion equation gives (4):

$$c = c_e \left(1 - \operatorname{erf} \frac{z}{2\sqrt{Dt}}\right) \quad (6)$$

for the vapor concentration at any level z at time t following a spill in a very tall enclosure;

$\operatorname{erf} \frac{z}{2\sqrt{Dt}}$ is the error function defined by

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx \quad (7)$$

and D (5) is the diffusion coefficient ($\approx 0.1 \text{ cm}^2/\text{sec}$ for UDMH and $0.13 \text{ cm}^2/\text{sec}$ for hydrazine).

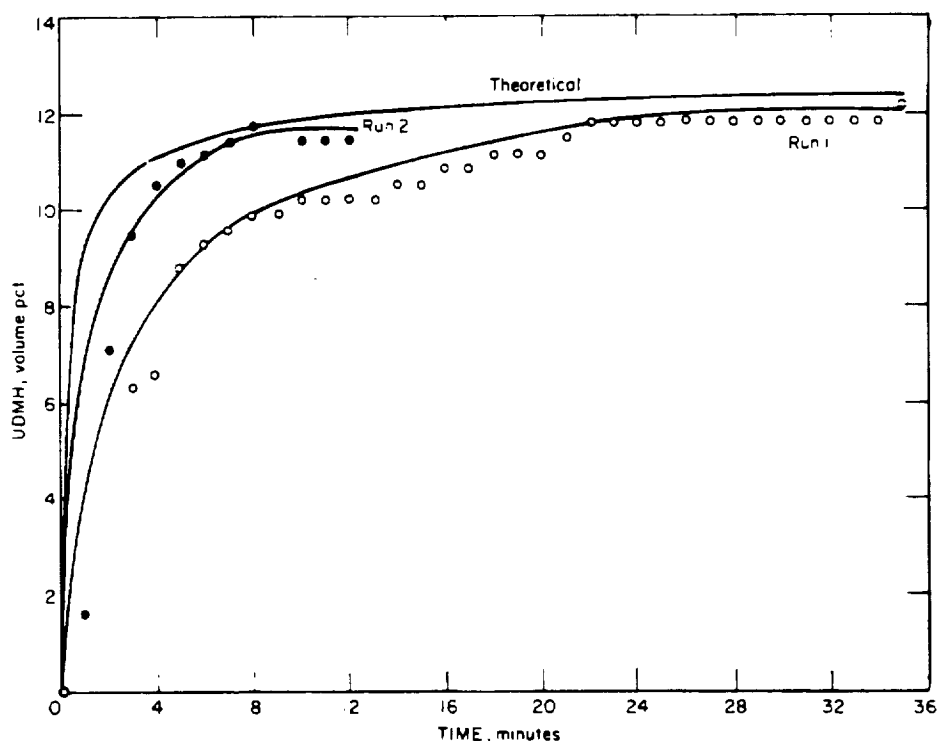


FIGURE 14. - UDMH Vapor Concentration in an Enclosed Space 1/2-inch Above a Pool of A-50 at About 72° F (22° C).

The applicability of the diffusion equation can be evaluated by comparing the results obtained at various heights as a function of time with those predicted by this equation. This has been done in figures 14 and 15. The first figure gives the concentrations of UDMH obtained 1/2 in. above a liquid pool of A-50 in a closed container. Samples were drawn into a 3.94-in. (10-cm) cell through a horizontal 3-in. ring equipped with eight 0.0135-in. holes and placed at the base of about 10 ft of 1/8-in. sampling line. The volume of the tubing and the cell was approximately 4 cu in.; with a sample flow rate of 6.4 cu in./min, as much as 3 minutes was required to obtain steady-state readings following the sudden exposure of the probe to a large quantity of UDMH vapor. The measured values appear to correlate fairly well with the values predicted by use of the diffusion equation, considering the slow response of the sampler and the Perkin-Elmer Model 21 spectrophotometer

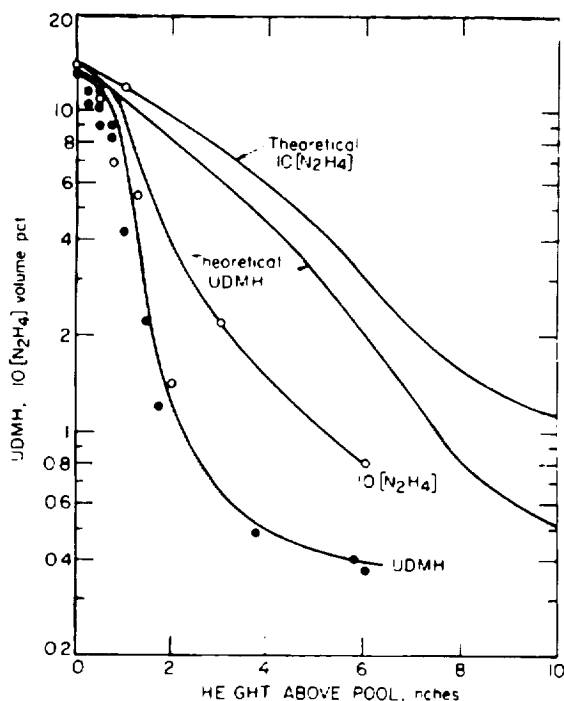


FIGURE 15. - UDMH and Hydrazine Vapor Concentration in an Enclosed Space 10 Minutes After Spillage of A-50 at About 75° F (24° C).

in., but not at such heights as 2 in. The convective disturbance in question is a slow layering current which carries the heavy UDMH-air mixtures horizontally across the floor of the test chamber.

In the case of an A-50 spill in the open (vaporization limited), the heavier-than-air vapors will spread at a rate determined in part by the liquid spill and vaporization rates and the motion of the surrounding air. When A-50 was permitted to drip into a 3-ft aluminum channel mounted at an angle of 10° to the horizontal, a flammable zone* formed at the point at which the liquid fell into the channel. This zone then moved down the channel at a relatively uniform rate ahead of the liquid. With a drip

*Determined visually by use of an electrical discharge to the aluminum channel (flat plate in subsequent experiments).

used for the analyses. Figure 15 gives the predicted and measured UDMH and hydrazine vapor concentrations 10 minutes after a spill. Again, the theoretical and actual curves are in fairly good agreement near the surface of the liquid (less than 1 in.) but the measured values fall below the predicted values at distances above 1 in.

We interpret this as follows: from equation (6) note that a specific vapor concentration, c , occurs at a constant value of z/\sqrt{t} . Thus with each doubling of height, z , the same concentration is attained only after fourfold longer intervals, t . This means that the diffusive flow rate of UDMH through each horizontal cross-section is falling off with the square of height. Diffusion is fast enough to compensate for a slow convective disturbance at small heights, like 1/2

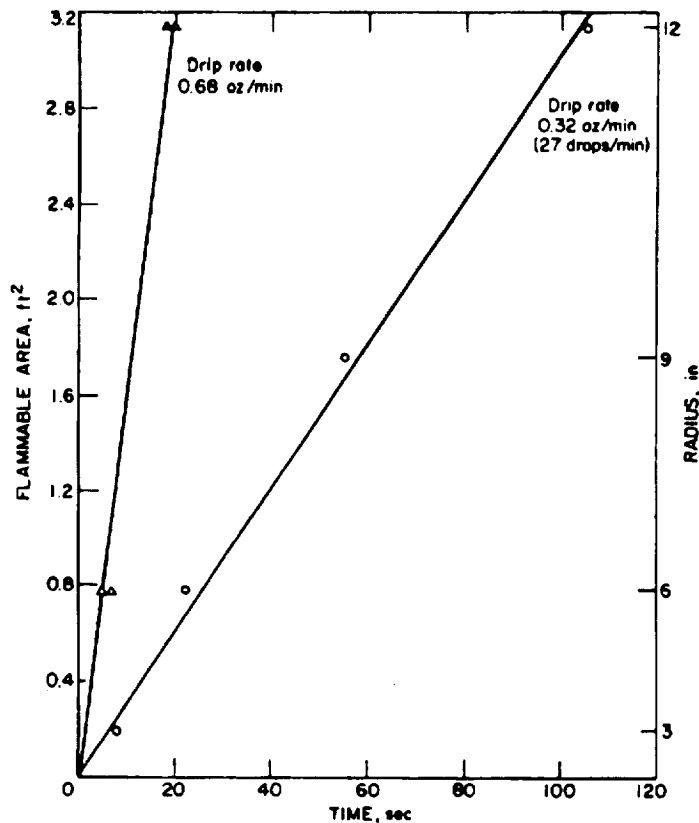


FIGURE 16. - Flammable Area Produced by A-50 Dripping on a Flat Plate.

rate of 0.14 oz/min (4 gms/min=12 drops/min) the flammable zone moved along the channel at 4.9 ft/min; with a drip rate of 0.46 oz/min (13 gms/min), the flammable zone moved at 13.4 ft/min. MMH gave similar results. When the A-50 dripped onto a horizontal flat plate, a flammable zone moved outward at such a rate that the areal coverage increased linearly with time. Thus with a drip rate of 0.32 oz/min (9 gms/min=27 drops/min) from a tube located 23 inches above the plate, the flammable zone spread outward at 1.8 ft²/min; with a drip rate of 0.68 oz/min (19.2 gm/min), the flammable zone spread outward at about 9.8 ft²/min. Determinations were made at distances to 12 in. from the point at which the A-50 impacted the flat plate (figure 16).

A high pressure leak was simulated by projecting A-50 and MMH through a Bete P-54 fog nozzle (see Task E). The liquid fuel recovered 10 in. from the nozzle is given in table 1. As expected, less fuel is recovered as the pressure is increased from 0 to 90 psi. Approximately 1/3 of the A-50 vaporizes in being projected 10 in. at an initial pressure of 60 to 90 psi. About 1/5 of the MMH vaporizes under the same conditions. The amount of fuel recovered at various distances from the above nozzle at an initial pressure of 30 psi is given in table 2. Again, as expected, the amount of fuel that appears in the vapor state increases as the distance, and therefore the vaporization time, increases.

4. Liquid Composition During Evaporation

A 10-in. diameter glass dish was nearly filled with 3.1 lbs of A-50 and an air flow of 150 ft/min was established across the surface. Liquid

TABLE 1. - Liquid Fuel Recovered 10 Inches
From Bete P-54 Nozzle

Pressure psi	A-50 weight percent	MMH weight percent
0	81	96
15	70	82
30	69	86
60	63	82
90	65	78

TABLE 2. - Liquid Fuel Recovered 1 to 20 Inches
From a Bete P-54 Nozzle at 30 PSI

Distance inches	A-50 weight percent	MMH weight percent
1	92	91
5	89	87
10	70	86
15	66	91
20	71	81

samples were taken with 200 microliter syringes just below the liquid surface and at 1/8-in. and 1/4-in. below the surface. The syringes were fixed in a jig to give a reproducible spacing. The liquid samples were titrated to give the results of table 3.

The scatter of data is far greater than the usual analytical uncertainties (about 0.1-0.2 percent UDMH). However, they do show the accumulation of water from the atmosphere which is concurrent with the depletion of UDMH. While there appears to be a slight composition gradient below the surface, this hardly appears to be formidable factor in establishing the evaporation rates.

5. Recommendations Relative to Task B

In case of an A-50 spill, about 30-40 percent of the liquid is readily vaporized (tables 1 and 2) giving vapor/air mixtures up to about 15 percent in fuel concentration. Since the vapors are mainly UDMH, any concentration above about 2 percent should be considered flammable.

The evaporation rate from a spill varies with only the square root of ventilation air speed; thus, any measure that improves

TABLE 3. - Analysis of Liquid From Evaporating
Pool of A-50

Time-Position	Material (Weight Percent)		
	N ₂ H ₄	UDMH	Water*
Before evaporation	51.8	46.6	1.6
Pool half evaporated			
Surface	78.0	9.6	12.4
	75.7	9.9	14.4
1/8 inch below	77.9	10.2	11.9
	57.4	5.9	36.7
1/4 inch below	75.7	12.2	12.1
	76.6	12.9	10.5
Pool 3/4 evaporated			
Surface	72.6	3.0	24.4
	67.8	1.6	30.6
1/8 inch below	74.2	3.0	22.8
	71.2	1.1	27.7
1/4 inch below	71.9	1.2	26.9

*By difference

ventilation rate will speed the dilution of vapors to concentrations below 2 percent. A pound of ventilation air per minute will eventually inert the evolved vapors from several square feet of exposed A-50 surface.

Very slow convection currents, velocities of a fraction of a foot per second, suffice to remove flammable vapor from all but the immediate vicinity of a spill surface (figure 15). But when these convection currents are induced by the density of the A-50 vapor, flammable concentrations may appear at some distance from a spill. The addition of Halon 1301 as inerting agent is also an effective countermeasure against this layering, since 20 percent Halon 1301/air is almost identical in density to 80 UDMH/20 N₂H₄ fuel vapors.

Task C - Carbon Dioxide Application

Although carbon dioxide is ordinarily considered an inert vapor, it forms a solid when it contacts A-50 and UDMH, and syrupy liquids when it contacts hydrazine and MMH; heat is evolved in each case (Task C-3). An elemental analysis of the reaction products proved inconclusive as a mass balance could not be obtained. However, by normalizing the experimental elemental weights the primary reaction products of carbon dioxide and UDMH, MMH and hydrazine appear to be $(\text{CH}_3)_2\text{NNHCOOH}$, $\text{CH}_3\text{NHNHCOOH}$, and $\text{N}_2\text{H}_3\text{COOHN}_2\text{H}_4$ respectively. Such compounds have been described by Audrieth and Ogg (3). The solid adduct of UDMH was not impact sensitive at the maximum drop height of 10.8 ft (330 cm) with an 11 lb (5 kg) weight.

A methane/oxygen pilot flame surrounded by a nitrogen sheath was used to determine the effectiveness of carbon dioxide in inerting the atmosphere above a 6-in. diameter pool of A-50 at room temperature. The same apparatus was used to determine the quantity of carbon dioxide needed to extinguish a fire burning above a 6-in. diameter pool of A-50. Between 29 and 33 percent carbon dioxide was needed in the ambient air to prevent ignition of the A-50 vapors by a methane/oxygen flame, and 35 percent was needed to extinguish the flame during the early stages of burning; this figure replaces the range of values (29-38 percent) obtained earlier. Extinguishment occurred abruptly, if at all, before the onset of the hydrazine burning (see Task D). Small concentrations of carbon dioxide in the atmosphere had little measureable effect on the burning rate of A-50 or of UDMH and hydrazine alone. Figures 17 and 18 show the weight loss against time of UDMH and of hydrazine and a hydrazine-water solution burning in air and in various carbon dioxide-air mixtures. In each case, these components of A-50 burn at rates that are virtually unaffected by the presence of the carbon dioxide except where extinguishment results (UDMH in 35 percent CO_2 /65 percent air).

The results of three experiments in which 12.2 fl oz (360 ml) of A-50 was placed in insulated 2.87 in. (7.3-cm) id x 3.34 in (8.5-cm) high glass cylinders within a 2-ft diameter by 4-ft chamber and exposed to CO_2 /air atmospheres containing 15, 30, and 100 percent CO_2 are summarized in table 4. In each case, liquid and gas temperatures

TABLE 4. - Temperature Rises Associated with A-50 Reacting with CO_2 in the Atmosphere

Initial T, °F	Percent CO_2	Maximum T, °F	
		gas	liquid
68	15	113	93
68	30	127	104
68	100	140	140

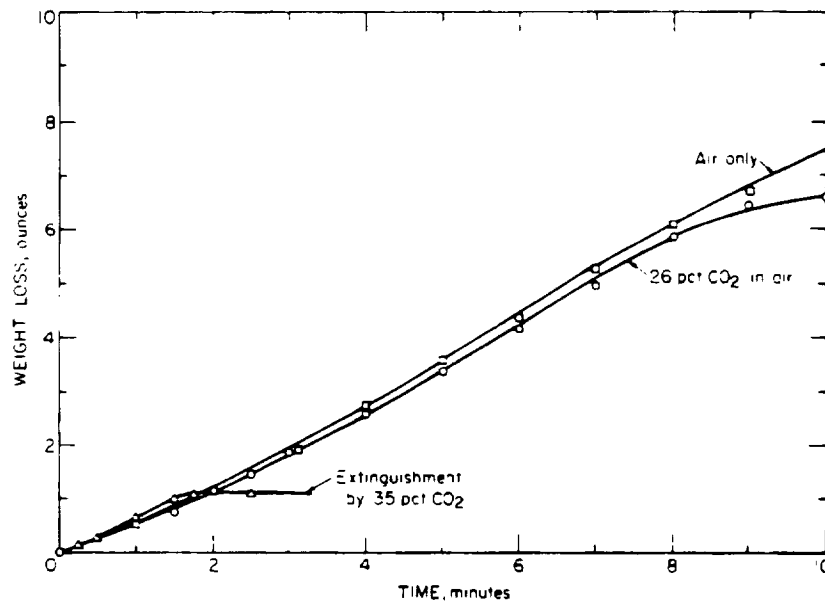


FIGURE 17. - UDMH Burning in Air-CO₂ Mixtures.

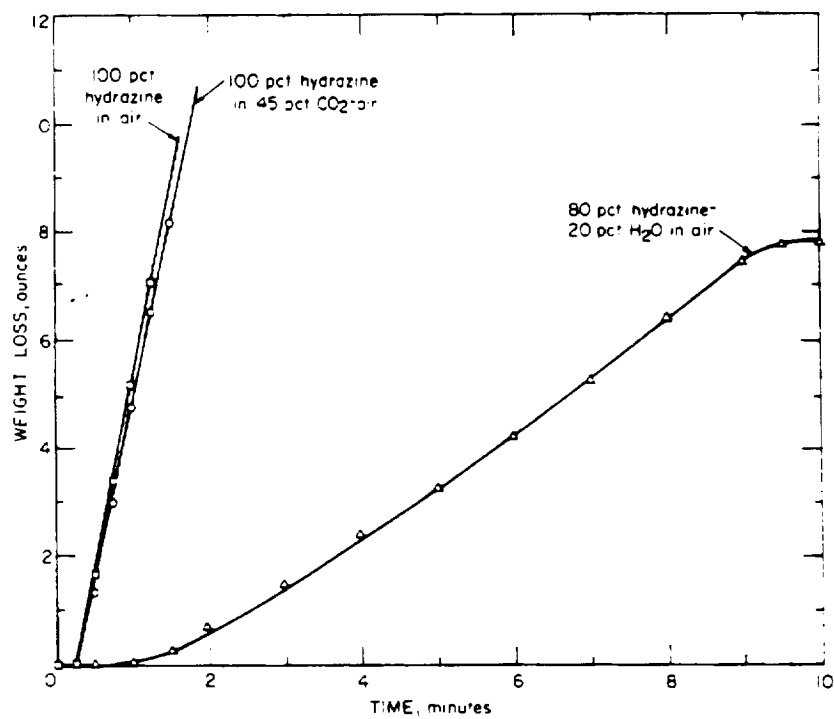


FIGURE 18. - Hydrazine Burning Rates with Diluents.

increased and the A-50 separated into two clear layers (Task C-1). During 2 to 4 hours exposure to the CO₂/air atmospheres, the samples lost only 4 to 6 grams, indicating that the evaporation and accumulation of CO₂ were nearly in balance. Figure 19 gives the temperature history for 40 minutes, above the liquid, just below, and 2.4 in. below the liquid surface when in contact with a 30/70 CO₂/air atmosphere.

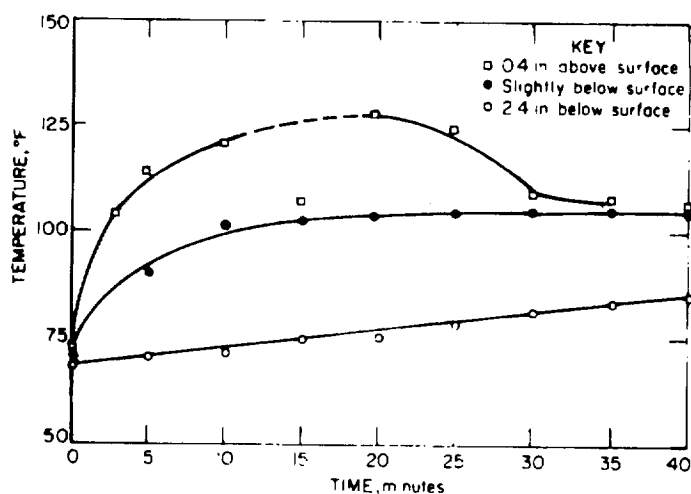


FIGURE 19. - Temperature History on Exposure of A-50 Pool to 30/70 CO₂/Air.

A demonstration was set up for motion picture documentation of the temperature rise of figure 19 and the layering of Task B. A one-pint sample of A-50 was poured into the usual 14-in. diameter tray which was supported a few inches above the floor of a 6 x 6 x 6 ft "cubical". An ignition source, either spark or flame, was located at some point on the cubical floor and did not ignite the vapors. Thereupon, a CO₂ fire extinguisher was operated remotely so that the visible vapor cloud (CO₂ plus condensed water) poured over the A-50 surface and then over the floor. Invariably, the cloud ignited and a flame slowly flashed back to initiate burning of the A-50 pool. The same result was obtained when powdered dry ice was sifted into the A-50 pool.

1. Recommendations Relative to Task C

We would not recommend the use of CO₂ for inerting of A-50 spills.

Task D - Inerting and Extinguishment with Combined CO₂ and Halon 1301

Earlier experience (10) had shown that CO₂ extinguishment of A-50 fires does not involve the unpleasant white smoke that occurs with extinguishment by Halon 1301; on the other hand, a pool of A-50 can be inerted by about 7 percent Halon 1301 as compared with 29-33 percent CO₂. It was a legitimate objective to determine whether some combination of CO₂ and Halon 1301 might not provide the best overall protection.

1. Inerting

The quick answer to this question is given by figure 20 which shows that any "synergism" in the performance of CO₂ and Halon 1301 is strictly unfavorable. The dashed curve shows, for example, that it requires more Halon 1301 to inert a pool when there is already 20 percent CO₂ in the atmosphere than with no CO₂.

An important dividend of this task was the confirmation of inerting by 7 percent Halon 1301 at 70-75°F. In our previous project, the A-50 pool comprised 50 ml of liquid fuel in a 4-in. diameter dish with a spark ignition source; in the present work, the A-50 was increased to 250 ml in a 6-in. diameter dish and ignition was attempted with a methane/oxygen torch impinging directly on the liquid. The required percentage of Halon 1301 for inerting was apparently identical.

2. Extinguishment

The burning of liquid A-50 is typical of the burning of fuel blends except for the monopropellant behavior of hydrazine. Figure 21 shows the radiation level and also the weight loss vs time for 90 lbs A-50 burning in a 48-in. diameter aluminum tray. There are clearly two stages: initially a diffusion flame which resembles the pool burning of UDMH and during which the first half of the weight loss occurs; thereafter a faster burning accompanied by vigorous agitation of the liquid. The radiant output of the fire is about 15-20 percent of the total thermal power during each stage of burning. No effective countermeasure was found for the second stage of burning except for dilution with copious quantities of water. However, the fire can be extinguished during the first stage by large concentrations of CO₂ or Halon 1301.

Burning rates were determined from the slopes of the weight loss vs time curves at tray diameters from 2-1/2 to 48 in. and the respective values for first stage and for second stage burning are plotted against tray diameter in figure 22. The first stage values are shown in relationship to the burning rates of pure UDMH (14) and are clearly similar to

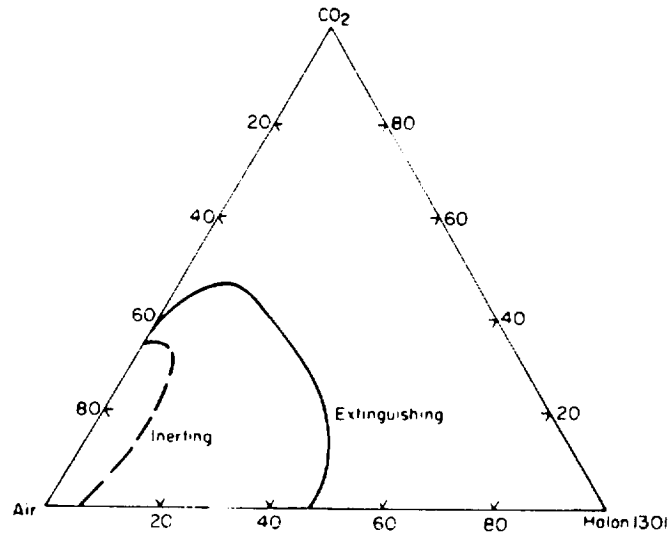


FIGURE 20. - Inerting and Extinguishment Requirements of A-50 in Air with CO₂ and Halon 1301.

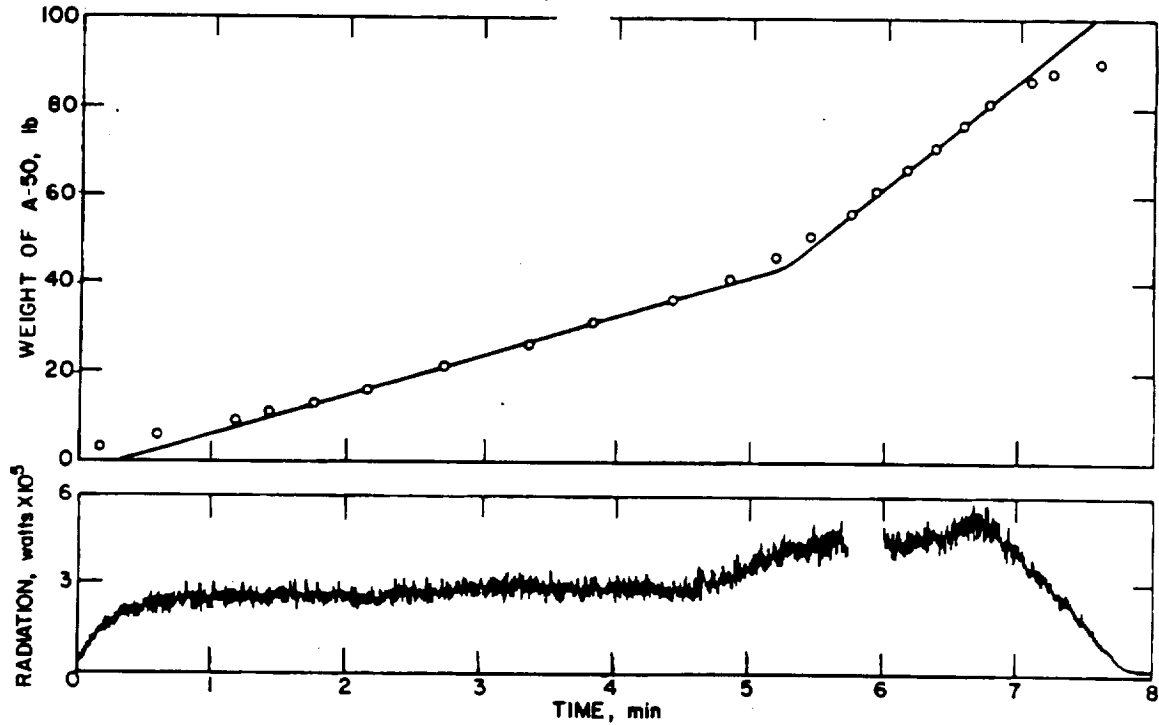


FIGURE 21. - Burning Rate of 90 lbs of A-50 in a 4-ft Diameter Aluminum Tray in Air.

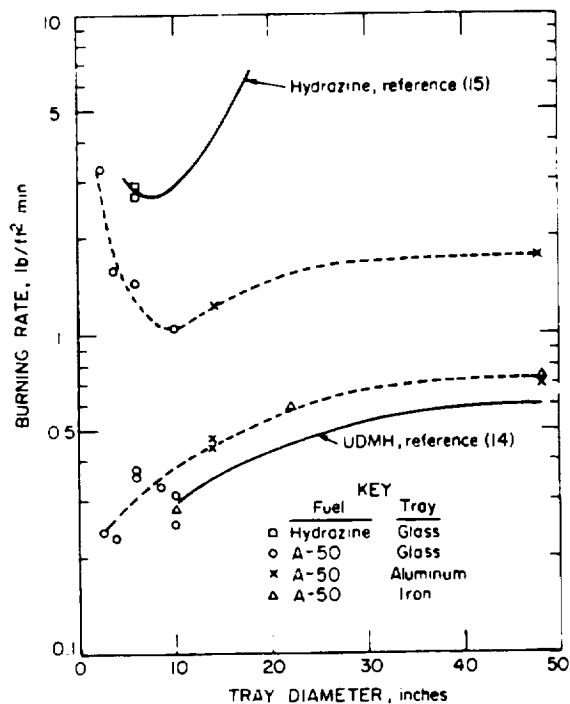


FIGURE 22. - Burning Rate of A-50 as Function of Tray Diameter.

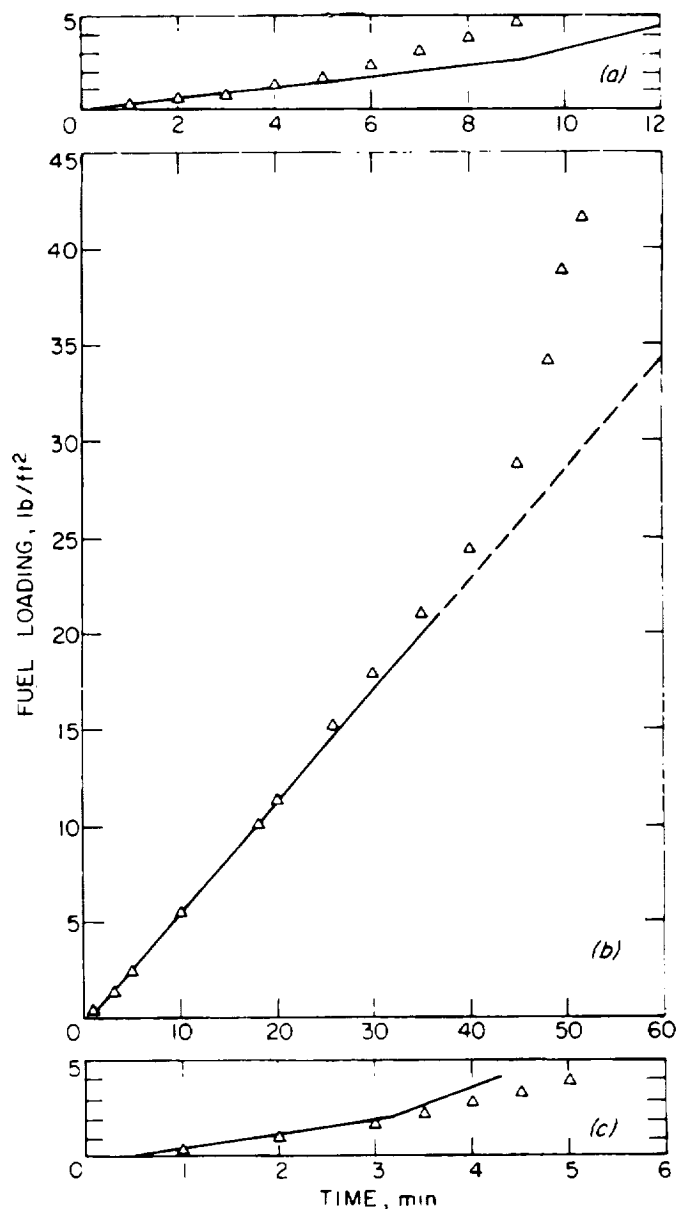


FIGURE 23. - Burning Rates of A-50 in Contact with Iron.

UDMH in dependence on pool dimension. The second stage rates, as shown in relationship to the burning rates of pure hydrazine (15) are fortunately of much lower magnitude. The three symbols used in figure 22 pertain to experiments with glass, steel and aluminum trays; there are no obvious differences in the initial rates of burning. However, there is something different about the burning of deep layers of A-50 in iron as is shown in figure 23. Discussion of this point belongs properly in Task F.

The addition of CO₂ to the ambient air has almost no effect on burning rate until, at 35 percent CO₂, a UDMH or first stage A-50 flame abruptly blows off. This was shown in figure 17. The effect of adding Halon 1301 is even more remarkable. At concentrations greater than perhaps 5 percent Halon 1301 the luminous diffusion flame disappears and the extinguishant then reacts directly with the hot fuel vapors, generating white smoke. But in the meantime, the weight loss rate is unaffected as shown in line 2 of table 5, and burning proceeds into the usual second stage. The required concentration of Halon 1301 to completely extinguish an A-50 fire is apparently a strong function of tray diameter; thus, 36 percent Halon 1301 sufficed for a 4-in. tray (10) but 48 percent is required to extinguish a 6-in. diameter pool fire. Since 48 percent is already an impracticable quantity of extinguishant, the work was not pursued with larger diameters of A-50 pool.

3. Recommendations Relative to Task D

Some extinguishments were carried out with mixtures of CO₂ and Halon 1301 and the critical concentrations plotted in figure 20. There is no apparent advantage to mixing these agents in any proportion.

TABLE 5. - Liquid Burning Rates in a 6-Inch Diameter Glass Tray (Air/CO₂/Halon 1301 Atmosphere)

Fuel	CO ₂ Volume %	Halon in Air	Burning Rate, lb/ft ² -min	
			Initial	Final
A-50	0	0	0.37	1.9
	0	19	.37	1.7
	20	20	.37	1.5
	35	0	0 (extinguished)	
UDMH	0	0	.31	.31
	26	0	.29	.29
	35	0	0 (extinguished)	
Hydrazine	0	0	2.9	2.9
	45	0	2.7	2.7

Task E - Water Sprays and Fogs

1. Reduction of A-50 Vapors

This was one of three competitive procedures for "sanitizing" a spill. The others were to form an addition compound with CO_2 (Task C) and to initiate a replacement of UDMH with ammonia (Task I).

Figure 24 shows the UDMH vapor concentration 3 in. from the edge of a pool of A-50 and 1/2 in. above the floor in a 10 percent Halon 1301/air atmosphere before and after addition of 1.76 lbs (800 gms) of a relatively fine water spray. The Halon 1301 was first added to the air in an upright cylindrical vessel (3 ft diameter by 4 ft) sealed at both ends with plastic sheets. One pint (0.94 lb)

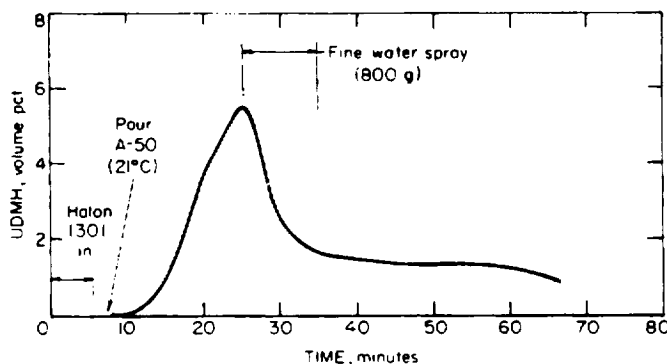


FIGURE 24. - UDMH Vapor Concentration 3 in. from a Pool of A-50 and 1/2-in. Above the Floor in a Halon 1301/Air Atmosphere Before and After Addition of Water Spray.

of A-50 was then poured into a 3/4-in. high by 14-in. diameter aluminum tray placed at the center of the floor of the cylindrical chamber. When the UDMH vapor concentration approached 6 percent, water was sprayed into the vessel for 10 minutes with a Bete PT-10 Fog nozzle (table 6) that was mounted 1 ft above the center of the A-50 pool. The water effectively removed the flammable vapors from the atmosphere and reduced the vapor pressure of UDMH and hydrazine in the A-50/water pool so that the vapors above the pool were no longer flammable (cf figure 13). UDMH vapor concentrations were determined by use of the sampling system and procedure described earlier (Task B-3). Similar results were obtained with 2.29 lbs (1040 gms) of water delivered as a coarse spray by a Bete PT-28 nozzle (figure 25). However, with 0.53 lb (240 gms) of water, the flammable vapor concentration was reduced for a brief period but remained in the flammable zone (figure 26); the total amount of water in this case was not enough to reduce the UDMH and hydrazine concentrations to a value below the lower limit (figures 1, 2, and 13). Accordingly, while a water spray may be effective in reducing the A-50 vapor content of the atmosphere to

TABLE 6. - Characteristics of Bete* Spray Nozzles

Water delivery rate at 60 psi, gal/ft ² -min			
Designation	Manufacturer's Specification	Into a 6-Inch Dish	Into a 14-Inch Dish
P-10	0.040	0.043	--
P-28	0.093	0.096	0.044**
P-54	0.133	0.133	0.066**

*Bete Fog Nozzle, Inc., 322 Wells Street, Greenfield, Mass. 01301
 **At 30 psi

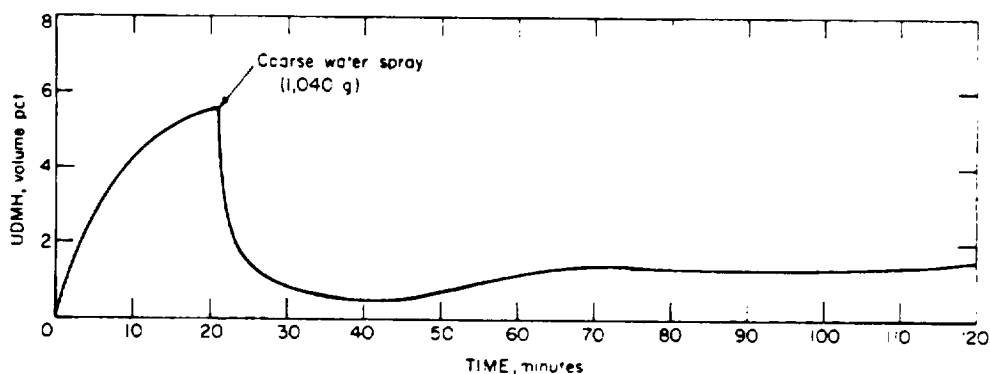


FIGURE 25. - UDMH Vapor Concentration 11 in. from a Pool of A-50 and 1/2-in. Above the Floor Before and After Addition of Water Spray.

a safe level, it will not remain in this state unless the A-50 liquid is diluted by twice its weight of water (cf Task A-1).

For purposes of comparison the same experiment was repeated using crushed dry ice instead of water spray. Figure 27 shows the UDMH concentration 3 in. from a pool of A-50 and 1/2 in. above the floor before and after the addition of 0.3 lb (137 gms) and 0.96 lb (437 gms) of carbon dioxide. The UDMH concentration dropped momentarily after each addition but quickly rose again.

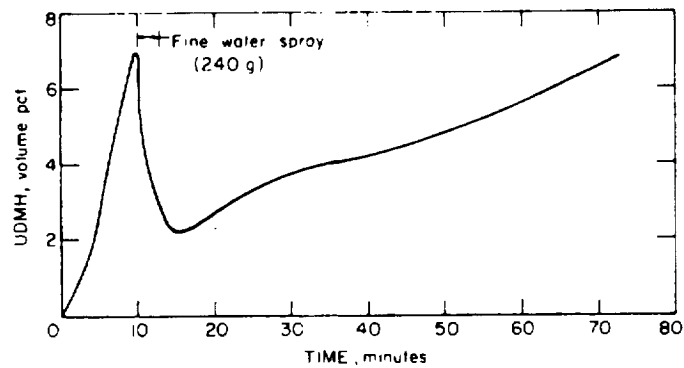


FIGURE 26. - UDMH Vapor Concentration 3 in. from a Pool of A-50 and 1/2-in. Above the Floor in a Halon 1301/Air Atmosphere Before and After Addition of Water Spray.

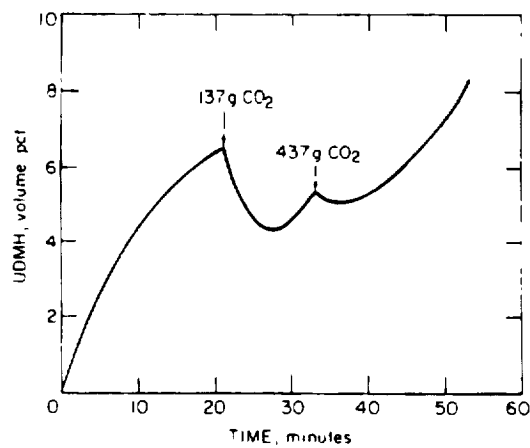


FIGURE 27. - UDMH Vapor Concentrations 3 in. from a Pool of A-50 and 1/2-in. Above the Floor Before and After Addition of Carbon Dioxide.

2. Fire Extinguishment by Water

A pertinent observation is that water decreases the burning rate of a UDMH or N_2H_4 fire whereas the gaseous extinguishants, N_2 , CO_2 and Halon 1301, have no apparent effect short of extinguishment. This is illustrated in figure 18 and also in columns 2 and 3 of table 8.

There are at least three procedures by which one might extinguish an A-50 fire with water: (1) One can add water to the liquid fuel in sufficient mole fraction that it concentrates with continued burning and the mixture eventually distills itself into the nonflammable zone of figure 5. Mixtures shown as points 3, 4 and 5 of figure 5 all burn to eventually nonflammable residues, points 3', 4' and 5'; a serious disadvantage is the long duration of burning by which the fire achieves its own lingering end. Test #10 of table 9 also illustrates the method: 10 lbs of A-50 were set afire in a 22-in. diameter tray and given 15 seconds preburn whereupon water was added at 12 lbs/min in a stream which mixed with the A-50; it required 1-3/4 minutes, that is, 21 lbs water, to extinguish the 10 lbs A-50. (2) One can also add water to the distilling fuel vapors at such a flow rate as to create a nonflammable mixture. In the 22-in. diameter tray, the burning rate is about 0.6 lb/ft² min during the early stage of fuel consumption (figure 22). In tests 11-14 of table 9, we have added a water fog at a weight ratio of about 2:1 to this rate of burning. Extinguishment occurred rather quickly in each of 3 tests with upwards of 1.3 lb/ft² min of water; however in test 13 with 1.1 lb/ft² min the fire burned to completion. The 2:1 weight ratio here is only accidentally the same as the weight ratio for inerting liquid A-50. (3) The burning rate (evaporation rate) can be slowed by application of water, thereby making the fire more susceptible to extinguishment by a gaseous extinguishant. The final column of table 8 shows the much reduced requirement of Halon 1301 to extinguish fires of water-diluted fuels. Moreover, it should also be possible to dilute the burning vapors with water in the presence of Halon 1301 extinguishant and this is the sense of table 7. In tests 3 and 5 with no Halon 1301, a water delivery rate of about 0.4 lb/ft² min sufficed only to build up nonflammable concentrations after about 90 seconds of burning; with a nominal 5 percent Halon 1301, tests 2 and 4, true extinguishment occurred at about the same rate of water application; with the same nominal Halon 1301 concentration, a spray of 0.14 lb/ft² min was ineffective while a 0.6 lb/ft² min spray gave fast extinguishment. These numbers may be compared with those of table 9 to show the contribution of the Halon 1301 to extinguishment.

TABLE 7. - Water-Halon 1301 Extinguishment Data for A-50 in a 14-Inch Tray Located in a 12-Ft Sphere

Run	Bete Nozzle	Nozzle Pressure	Water Delivery Rate to 14-Inch Tray lb/ft ² min	Halon 1301 In Air vol %	Preburn Time, sec	Time to Extinguish Flame sec
1	P-54	60 psi	.57	5.6	8	12
2	P-28	30 psi	.38	4.8	7	16
3	P-28	30 psi	.38	0	10	83
4	P-28	30 psi	.43	5.0	26	37
5	P-28	30 psi	.43	0	30	64
6	2 P-10's	90 psi	.14	5.5	15	108

TABLE 8. - Burning Rates and Minimum Halon to Extinguish Water-Diluted Pool Fires

Fuel	Added Water %	Burning Rate g/cm ² min	Minimum Halon to Extinguish, %
A-50	0	.17	48
	20	.10	16
	50	.056	2.5
	64	No Ignition	
MMH	0	.15	40
	20	.071	14
	40	.058	2.5
	70	No Ignition	
Hydrazine	0	1.3	>50
	20	.21	18
	40	.061	2.5
	50	No Ignition	

TABLE 9. - Extinguishment of 10 Pounds A-50 After 15
Second Preburn in 22-Inch Diameter Tray

Test No.	Water Delivery Rate	Time to Extinguishment (sec)
10	4.6 lbs/ft ² min (coarse spray)	105
11	1.44 lbs/ft ² min (fine spray)	15
12	1.37 lbs/ft ² min (fine spray)	17
13	1.14 lbs/ft ² min (fine spray)	No extinguishment
14	1.37 lbs/ft ² min (fine spray)	21

3. Recommendations Relative to Task E

The basic factor reported here is that a mixture of two parts by weight of water to one part by weight of A-50 is not flammable under any normal circumstances. Therefore a water spray or fog can be used to "knock down" a concentration of vapors from A-50; it can also be used to put out a pool-supported fire without the necessity of inerting all of the A-50 in the pool.

Task F - Corrosive Characteristics

This task was terminated by a change-of-scope amendment on June 30, 1968 after the results given below had been obtained. One specific uncertainty that had led to the inclusion of the task in the plan of work was the unknown effect of iron oxides on the pool burning of A-50. Many of the surfaces exterior to the launch vehicle were of zinc-coated steel and corrosion studies had already shown that the organic zinc coating was not impervious to A-50.

The pool burning of A-50 in contact with various iron vessels is illustrated by figure 23. In figure 23a the burning of A-50 in a cast iron frying pan (triangles) is shown to start at about the same rate as in a glass casserole (broken line) of the same, 10 in.-diameter. However, the consumption rate increases in the iron pan and remains faster than in glass even though there is no evidence of second-stage (hydrazine) burning. The amount of fuel ignited in each case was about a one-in. depth.

The above experiment was then repeated, figure 23c, using 48-in. diameter steel and aluminum trays. Again the initial depth of fuel was about one in. in each tray. The initial burning rates were again about equal; thereafter the rate increased in the steel tray but not as

fast as was given by the second-stage burning of A-50 in aluminum. Thus the burning rate in contact with iron seems to be time-dependent in some different way than is given by the UDMH and N_2H_4 stages of burning in glass and aluminum.

Figure 28b shows the burning rate of 114 lbs of A-50 in the bottom section of a 22-in. diameter steel drum. The weight loss is initially linear with time, (0.60 lbs/ft² min) and nearly half the fuel is consumed before there is much acceleration of burning. Thereafter, burning continues to accelerate until the rate has increased by an order of magnitude (6 lbs/ft² min) in the final few minutes of burning.

At all three tray diameters, the initial burning rates (triangles) are quite consistent with the curve given in figure 22 for unblended UDMH. The final burning rate is never as high as is given by the curve for pure hydrazine in figure 22; however, we did approach this level after consuming about a 10-in. depth of liquid in the course of nearly an hour's burning.

1. Recommendations Related to Task F

While the experiments did uncover a new mode of burning in which the container surface played some indisputable part, we find no particular reason for alarm. If the anticipated A-50 spill is to involve great depths of liquid, it should not be permitted to burn for many minutes before water deluge is invoked. Consequently, the data present no reason to expect that burning rates on iron should be higher than on aluminum surfaces.

Task G - Combustion Products

In an earlier assignment, we had particular difficulty with the white smoke that developed when Halon 1301 was used to extinguish a diffusional (pool) fire. Various smoke samples gave varying weight percentages of fluorine and bromine and it was thought that the smoke varied in composition with its point of collection relative to the hot zone of the fire. Accordingly, we set up to burn premixed A-50/air in a Bunsen-type burner in which Halon 1301 was added at various concentrations to the air stream.

It turned out that smoke evolution from any premixed A-50/air/Halon 1301 flame was almost too scanty to observe. But the experiments with homogeneous mixtures were interesting in another context. Thus,

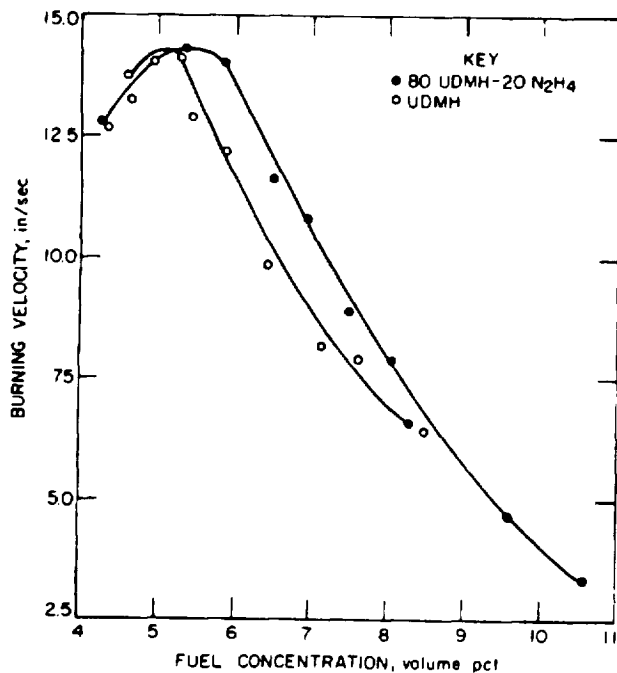


FIGURE 28. - Burning Velocities of A-50 Fuel Type/Air Flames.

to be several times more effective than nitrogen; in each case the effectiveness decreased markedly with fuel-rich mixtures. This is in line with the results of figure 20 which shows a marked difference in the effectiveness

the burning velocity of UDMH and of an 80 percent UDMH/20 percent hydrazine mixture were determined in air. The results are given in figure 28. As the peak burning velocity (14 in./sec) is about the same as that of the hydrocarbons, the effects of the Halon 1301 on A-50 can be compared to the effects of the Halon on methane. This is done in figure 29 in which the burning velocities of methane/air/Halon 1301 are plotted on the same scale as the burning velocities of the 80 percent UDMH/20 percent hydrazine mixture. While the burning velocity decreases linearly with Halon concentration in each case, the Halon is not as effective against the 80/20 mixture as it is against methane. Its effectiveness is more nearly that of the Halon against ammonia/oxygen/nitrogen flames (table 10). However, the tabulated data also show the Halon

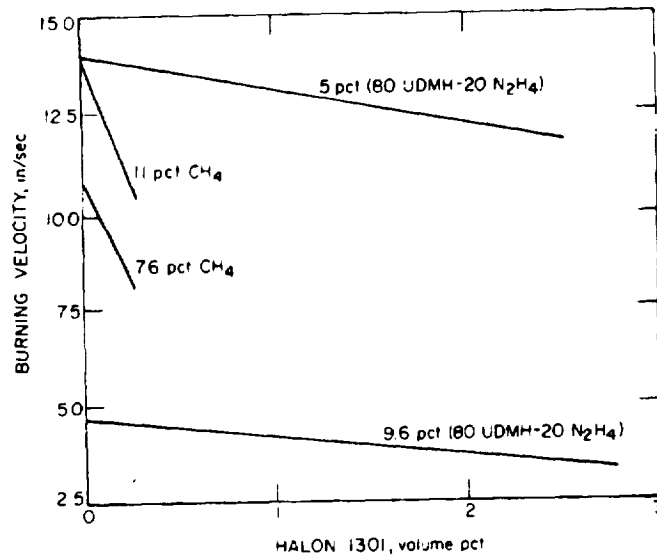


FIGURE 29. - Reduction of Burning Velocity by Halon 1301.

TABLE 10. - Reduction of Burning Velocity by Additives
Premixed with (80 UDMH - 20 N₂H₄)/Air

Additive	Fuel-Air Concentration, percent fuel	Burning velocity reduction/ percent additive
		cm/sec, %
Halon 1301	5.0	7.2
Halon 1301	6.2	6.2
Nitrogen	6.2	1.5
Halon 1301	8.2	3.2
Nitrogen	8.2	.5
Halon 1301	9.6	1.2
Halon 1301	11.1 (CH ₄ /air)*	30.0
Halon 1301	7.6 (CH ₄ /air)*	25.0
Halon 1301	32-39(NH ₃ /O ₂ /N ₂)*	10.0

*Rosser, W. A., H. Wise, and J. Miller. Seventh Symposium (International) on Combustion, 1958, Butterworths Scientific Publications, London, pp. 175-182.

of the Halon as an inerting agent as opposed to its use as an extinguishment agent.

The data in table 11 show the effect of adding nitrogen, carbon dioxide, and Halon 1301 to the secondary air stream around a rich (8.2 percent) flame of (80 UDMH-20 N_2H_4)/air. This secondary air can be entirely replaced by nitrogen or by as much as 79 percent carbon dioxide without measureable effect. However replacement of 48-50 percent of the air with Halon 1301 results in an appreciable reduction in the burning velocity and blowoff of the flame. This indicates that the extinguishment of A-50 pool fires by 40-50 percent Halon 1301 has some fundamental basis.

The combustion products that were formed when A-50 burned in a 1.2-in. pyrex dish located in a glass combustion chamber were collected and analyzed. Approximately 0.35 fl oz of A-50 was burned in various Halon/air atmospheres. The gaseous products found 5.9 and 0.24 in. above the burning pool were analyzed by gas chromatographic methods. The results are given in tables 12 and 13. In the absence of Halon, the combustion products are air, nitrogen, carbon dioxide, water and hydrogen. With Halon, hydrocarbons are formed in the initial stages of burning (see column 3, table 12 and columns 2 and 4, table 13) while ammonia and additional hydrogen are formed in the final stages (see column 4, table 12 and column 3, table 13). Elemental analyses (table 14) and the X-ray diffraction patterns of the solids showed these to be primarily ammonium bromide (table 15) with traces of carbon, ammonium fluosilicate and sodium fluosilicate. The data in table 14 show that only a very small amount of the available fluorine appeared in the smoke, accordingly, the above experiments were repeated in a plastic combustion chamber in an effort to determine the fate of the fluorine in the combustion products; part of the fluorine in the Halon 1301 is to be found in the glass used to form the combustion chamber in the first experiment, and presumably part is to be found in the unidentified peaks listed in tables 12 and 13. All the gases were collected in distilled water and the fluorine content was determined by thorium nitrate titration. The fluorine content of the solids was determined by first distilling the fluorine as fluosilicic acid and then by thorium nitrate titration of the distillate. In these experiments, approximately one percent of the available fluorine was found in the reaction gases and solid residue as fluoride (presumably HF in the gas phase) with the major part in the gaseous state; approximately four percent of the available bromine was found in the solid residue (table 16). No evidence of carbonyl fluoride was found.

TABLE 11. - Effect on Burning Velocity of Rich (80 UDMH/20 N₂H₄)/Air Flame, Halon 1301, and CO₂ in Secondary Air Streams

<u>Composition of secondary stream, percent</u>		<u>Laminar burning velocity, cm/sec</u>
<u>Additive</u>	<u>Air</u>	
0	100	18.9
100 N ₂	0	18.9
38 CO ₂	62	19.3
79 CO ₂	21	19.3
25 Halon	75	18.9
41 Halon	59	17.9
48 Halon	52	11.2
50 Halon	50	Blowoff

TABLE 12. - Gaseous Products 5.9 Inches Above Surface of A-50 Pools Burning in a 1.2-Inch Diameter Pyrex Dish

<u>Stage of Burning</u>	<u>Initial</u>	<u>Initial</u>	<u>Final</u>
<u>Halon Concentration, %</u>	<u>0</u>	<u>25.4</u>	<u>14.9</u>
H ₂	0.1	3.5	12.4
O ₂	17.5	16.7	8.5
N ₂	80.1	66.2	48.3
CH ₄	.0	4.1	.2
CO	Tr	.2	Tr
CO ₂	1.8	.1	Tr
C ₂ H ₄	.0	.2	Tr
C ₂ H ₆	.0	.3	.0
Halon 1301	.0	6.9	2.3
H ₂ O	.5	1.2	.3
NH ₃	.0	.0	27.0
Unknown peak (est.)	.0	.6	.9

TABLE 13. - Gaseous Products 6 mm Above Surface of
A-50 Pools Burning in a Pyrex Dish,
1.2 in. id x 1.6 in. Depth

Stage of Burning	Initial	Final	Initial
Halon Concentration, %	25.4	25.4	33.8
<u>Gas Composition</u>			
H ₂	8.8	18.8	13.2
O ₂	13.4	3.7	5.0
N ₂	61.1	41.9	42.5
CH ₄	5.2	8.5	15.9
CO	.4	.3	.7
CO ₂	.1	Tr	.1
C ₂ H ₄	.3	.3	.7
C ₂ H ₆	.3	.4	.9
Halon 1301	7.7	6.1	15.9
Unknown peak (est.)	.4	2.0	3.0
H ₂ O	1.4	.4	2.0
NH ₃	.8	17.6	.0

TABLE 14. - Analyses of Smokes from A-50 and MMH Pool
Fires in Contact with Halon 1301

Fuel	A-50	A-50	A-50	A-50	A-50/H ₂ O (80/20)	A-50	MMH
Stage of burning	Initial	Initial	Initial	Initial	Initial	Final	Initial
Halon 1301 %	14.9	25.4	25.4	33.8	14.9	14.9	25.4
Carbon	0.21	0.05	0.06	0.17	0.10	0.10	1.35
Hydrogen	3.93	3.94	4.06	(5.08)	3.96	3.86	3.96
Nitrogen	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Fluorine	0.29	0.22	0.31	0.40	0.35	1.78	0.60
Bromine	73.2	73.5	67.7	72.2	65.8	66.0	67.0

TABLE 15. - Rates of Ammonium Bromide Production from A-50 and MMH Pool Fires in Contact with Halon 1301

Fuel	Halon 1301 %	NH ₄ Br mg/sec	Fuel Consumption cc/sec
A-50	14.9	3.53	0.0442
A-50	25.4	6.41	.0507
A-50	33.8	7.22	.0499
A-50/H ₂ O (80/20)	14.9	4.15	.0480
A-50/H ₂ O/NaCl (80/18/2)	14.9	3.72	.0384
A-50/H ₂ O/NaHCO ₃ (80/18/2)	14.9	3.91	.0417
MMH	25.4	3.5	.0301

TABLE 16. - Products Produced by the Combustion of A-50 in Freon-Air Atmospheres in a Nickel Crucible Housed in a Plastic Chamber

A. Input

Run	Wt A-50 Burned gms	Air Flow		Freon Flow		Freon in Air	Available F Br	
		cc/sec	ft ³ /min	cc/sec	ft ³ /min	%	gms	
10	8.08	315	0.67	33.5	0.071	9.6	10.2	14.1
11	8.08	145	0.31	60	0.13	29.3	16.3	22.6
12	8.08	145	0.31	60	0.13	29.3	16.3	22.6

B. Combustion Products

Run	Burn Time sec	Recovered		% Recovered		F	Br	mg F	mg Br
		F, mg	Br, mg	F	Br	mg/sec	mg/sec	gm A-50	gm-A50
10	135	71.3	528	0.7	3.7	0.53	3.9	8.8	65.3
11	120	159.6	982	1.0	4.3	1.33	8.2	19.7	122
12	120	189.0	954	1.2	4.2	1.58	8.0	23.4	118

Task H - Test of Halon 1301 System

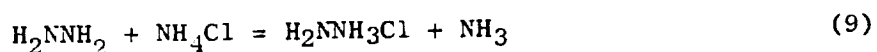
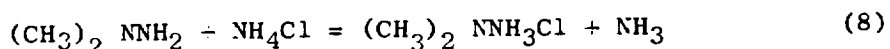
The original intention was that the Bureau of Mines should play an important role in the monitoring of Halon 1301 atmospheres during (mock-up) tests of dispersal systems. However, it turned out that multi-channel instrumentation was available with the Federal Aviation Agency who had already successfully applied it to Halon 1301 distribution studies in aircraft. Since the FAA consented to contribute both the equipment and the skilled operating personnel for the test series, the Bureau's part in this task was minimal.

The loss of visibility in the SLA during admission of Halon 1301 led to our final Task J.

Task I - Neutralization with Ammonium Salts

The failure of CO₂ neutralization (Task C) seemed to involve a matter of reaction rates in a heterogeneous system. Thus there was no doubt that an adduct formed, such as (CH₃)₂NNHCOOH, which tied up UDMH; however, the rate of disappearance of UDMH seemed to be slow; in the meantime, heat generated in forming the adduct served to vaporize unreacted UDMH so as to create flammable mixtures that would otherwise not have existed.

It was reasoned that a better scheme might involve the replacement reactions of A-50 with ammonium salts, as for example



which must surely go to the right because of the volatility of ammonia. It was also expected that the reactions might be slightly endothermic which would lead to a cooling of the A-50.

These expectations were confirmed on a small scale in which ammonia was liberated vigorously and the final product appeared to be a dry powder. When the procedure still looked feasible on a scale of several pounds A-50 and an equal weight of ammonium carbonate, the amendment of June 20, 1968 was suggested by which this line of work should supplant Task F.

The first test thereafter was to carry out the above reaction in the modified Cleveland open cup flash point tester. It turned out then that the residual powder was ignitable and stayed ignitable for about 30 minutes. The igniting gas mixture was evidently ammonia with some UDMH.

Finally, the UDMH concentration was monitored around an A-50 pool (figure 30) while ammonium carbonate was added. Figure 30 should be closely comparable to figure 27 in which the same weight of A-50 was treated with powdered dry ice. The result is again disappointing; the amount of UDMH in the pool had surely been reduced and its temperature had fallen nearly 20° F but the UDMH vapors were still widely distributed because of the ammonia which served as carrier gas.

A variety of ammonium salts were used in comparable experiments before the technique was finally discarded.

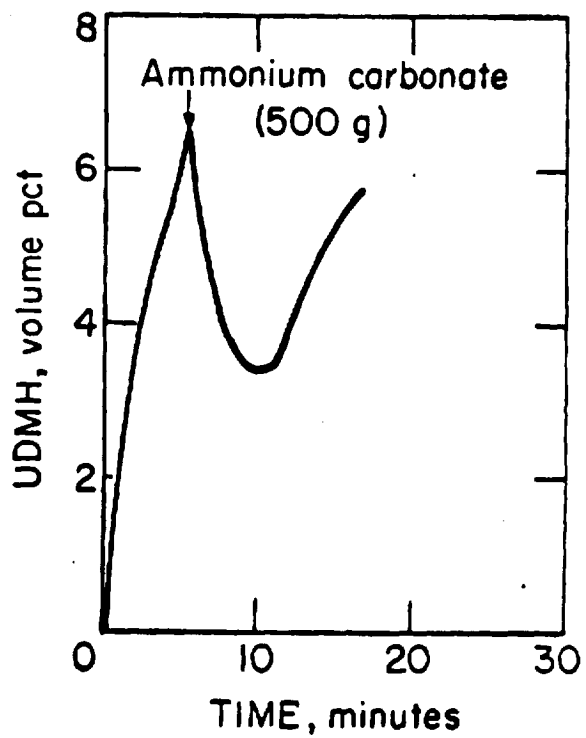


FIGURE 30. - UDMH Vapor Concentration
3 in. from a Pool of A-50 and 1/2-in.
Above the Floor Before and After
Addition of Ammonium Carbonate.

Task J - Halon 1301 Discharge Tests

The completion date of Tasks A-I was July 31, 1968 and a final briefing was held at Cape Kennedy on August 10, 1968. At that time, the NASA testing of Halon 1301 discharge systems was still in progress using a SLA mock-up of 2000 cubic feet and 85 pounds of liquid Halon 1301 pressurized with 600 psi nitrogen. The distribution of extinguishant though the volume of the SLA was entirely satisfactory (two point injection) but the visibility in the chamber was severely limited from the moment of Halon release. The fog was presumed to be atmospheric moisture which had condensed on contact with cold Halon 1301.

The NASA purchase request was amended on September 13, 1968 to permit a series of small-scale tests at the Bureau of Mines of the release of preheated Halon 1301. By table 17, if Halon 1301 is loaded into a constant volume system at a density of 17 lbs/ft³ and then heated beyond critical temperature (152° F) to 160° F its pressure should be 480 psia. Instantaneous release of the superheated vapor, presumably at constant enthalpy, should give expanded vapor at atmospheric pressure and 70° F (table 18). Since the dew-point of the conditioned air in the SLA is nominally 43° F there should be no general fogging of the chamber.

However, it was pointed out by refrigeration experts that some transient fogging might still be expected, since the last Halon 1301 to leave the pressure vessel must necessarily have done some work (enthalpy loss) in dispersing earlier fractions against the atmosphere. Accordingly, the Bureau of Mines was asked to carry out small-scale releases of Halon 1301 (5 lbs extinguishant in 128 cubic foot mock-up) with motion picture coverage.

The Freon 1301 was contained in a tank that had a volume of 0.377 cubic feet and a 1-inch discharge pipe. Discharge was accomplished by rupturing a diaphragm in the discharge line with an electric detonator. The tank pressure during discharge was observed with a pressure transducer in the tank and a direct writing oscillograph. The tank was preheated to as much as 170° F by immersion in a heated water bath.

The Freon 1301 was discharged into the top of a 4-foot square by 8-foot high chamber which had a transparent front cover to permit motion picture coverage of the discharge; all experiments were photographed at 80 frames per second. The atmosphere in the box was controlled to approximately 75° F and 43 percent relative humidity as shown in columns 2 and 3 of table 19.

Experiments were conducted at two initial Freon 1301 temperatures, 75° F and 160° F, and with two liquid Freon 1301 loadings 5.5 and 11.8

TABLE 17. - Pressure and Enthalpy of Superheated
Halon 1301 Vapor at 160° F*

<u>Volume</u> <u>(cu ft/lb)</u>	<u>Density</u> <u>(lb/cu ft)</u>	<u>Pressure</u> <u>(psia)</u>	<u>Enthalpy</u> <u>(BTU/lb)</u>
0.0799	12.5	400	63.18
.0687	14.5	440	62.01
.0589	17.0	480	60.67
.0501	20.0	520	59.07
.0415	24.0	560	56.99
.0317	31.5	600	53.54

*Taken from "Superheated Vapor" table of Publication
T-1301 of E. I. du Pont de Nemours & Company, Inc.

TABLE 18. - Enthalpy as Function of Temperature
of Halon 1301 Vapor at
One Atmosphere*

<u>Temperature (°F)</u>	<u>Enthalpy (BTU/lb)</u>
40	57.3
60	59.5
80	61.7
100	64.0

*Interpolated from "Pressure-Enthalpy Diagram-
Freon Fe 1301" publication T-1301 of E. I. du Pont
de Nemours & Company, Inc.

pounds in the tank. The experimental conditions and results are summarized in table 19. It can be seen that all the superheated Freon 1301 shots resulted in a fog-free discharge whereas the discharges at ambient temperature all produced dense fog. Motion picture sequences of the experiments were forwarded to KSC during the performance of the task in October 1968.

TABLE 19. - Results of Freon 1301 Discharge from 0.37
Ft³ Cylinder into a 128 Ft³ Chamber

Test	Chamber		Freon 1301			Discharge Time second	Result
	Temperature ° F	Relative Humidity percent	Temperature ° F	Pressure psig	Density lb/ft ³		
1	75	41	140	395	14.7	0.72	No fog
2	72	44	160	440	14.7	0.83	No fog
3	73	42	160	440	14.7	0.70	No fog
4	75	44	75	215	14.7	0.95	Fog
5	75	45	75	214	14.7	0.87	Fog
6	75	45	75	214	14.7	0.85	Fog
7	74	44	160	396	15.6	0.75	No fog
8	75	41	75	212	14.7	0.80	Fog
9	73	40	160	425	14.7	0.70	No fog
10	75	45	81	232	31.2	0.80	Dense fog for ≈ 4 min
11	75	42	160	585	31.2	0.65	No fog

III SUMMARY AND CONCLUSIONS

A. The propellant Aerozine-50 poses severe fire and explosion hazards unless unusual measures are taken for inerting and for fire extinguishment.

1. The vapor pressure of A-50 is equivalent to a 15 percent fuel vapor/air mixture at 77° F and 1 atmosphere.
2. A-50 vapor/air mixtures are flammable at concentrations above 2-2.6 percent; there is effectively no upper limit of flammability.
3. The density of the fuel vapor is about twice that of air, which induces convective currents; fuel vapor concentrations are thereby reduced in the immediate vicinity of a spill but the hazard is introduced of flammable mixtures at distant locations below or downwind of the spill.
4. Any scheme to improve ventilation will hasten the dilution of vapors to a concentration below the lean limit.

B. Water is the only agent which was effective in all aspects of inerting and extinguishment that were studied in this program.

1. The concentration of A-50 vapors in a compartment can be quickly reduced by water spray.
2. The flammability of liquid A-50 can be eliminated by dilution of the liquid with twice its weight of water.
3. The hypergolic ignition of A-50 by N_2O_4 can be prevented by dilution with large volumes of water.
4. A-50 fires can be extinguished:
 - (a) By addition of water in bulk to the liquid phase, extinguishment occurring when the water comprises two thirds of total weight.
 - (b) By training a fine spray on the burning surface, extinguishment occurring immediately if the fuel vapor/water mixture is nonflammable.
 - (c) Water and Halon 1301 are extremely effective in combination.

C. Halon 1301 provides a valuable possibility of preventing A-50 fires by inerting but cannot be counted upon to extinguish an A-50 fire because of the high concentrations that would be required.

1. Approximately 2 percent Halon 1301 will prevent secondary fires of many flight vehicle combustibles (mylar, velostat, polyurethane foam) which fires might be initiated by minor incidents involving the hypergolic propellants.

2. Approximately 5 percent Halon 1301 will prevent most other secondary fires. Also, 5 percent Halon 1301 reduces significantly the flow of water required to extinguish an A-50 pool fire.

3. Approximately 7 percent Halon 1301 prevents the spark or pilot flame ignition of A-50 at 72° F in pool diameters ranging from 4 to 14 inches.

4. A 20 percent Halon 1301/air mixture has the same density as fuel vapor of the composition 80 UDMH-20 N₂H₄; all layering problems should be alleviated by such concentrations of extinguishant.

5. It requires 40-50 percent Halon 1301 in air to extinguish an existing pool fire or to inert the richest possible vapor/air mixture at 77° F.

6. The white smoke observed on contact of Halon 1301 with A-50 fires is largely ammonium bromide. As such it does not present a serious toxicity problem, but visibility is greatly impaired. The gaseous combustion products include hydrogen fluoride; bromine has also been observed but not carbonyl fluoride.

D. We found no useful inerting or extinguishment technique based on either the mildly exothermic reaction of CO₂ with A-50 or on the endothermic replacement reactions of ammonium salts with A-50.

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Technical Report No. ASD-TR-61-716 of Flight Accessions Laboratory, Wright-Patterson AFB, Dayton, Ohio, May 1962.

APPENDIX I

Tasks

NASA Request Number CC-59100

Task A. Determine the water dilution ratios to prevent ignition of the fuels (A-50 and MMH) and also to prevent hypergolic reactions between the fuels and the oxidizer (N_2O_4).

Task B. Determine the evaporation rates, vapor distribution and liquid composition gradients for A-50 and MMH when dispersed in the following manner:

1. Pool,
2. Spray,
3. Drip,
4. Trickle

Task C. Determine the following characteristics when carbon dioxide is applied to spills of A-50 and MMH:

1. Chemical analysis of both gaseous and solid products.
2. Quantities required in air to neutralize fuel vapors and to extinguish fuel fires.
3. Temperature gradients resulting from the reactions.

Task D. Determine the inerting and fire extinguishing properties when CO_2 is used in a Freon 1301 inerting atmosphere in the presence of a fuel spill and a fuel fire.

Task E. Determine the effect of using water aerosols in a Freon 1301 atmosphere to reduce fuel vapors.

Task F. Determine the corrosive characteristics of A-50, MMH, and N_2O_4 when diluted with water on typical materials used for the launch vehicle outer skin. Discontinued by Amendment Number 1 dated June 20, 1967 to Purchase Request Number CC-59100.

Task G. Determine the products of combustion both quantitatively and qualitatively whenever possible.

Task H. Assist as required in the design and instrumentation of a series of tests to determine the rate of change of concentration gradients when Freon 1301 is introduced into a LM/SLA mock-up. Approximately 20 percent Freon concentration within a few seconds is desired throughout the cavity. The full scale mock-up, located at KSC, will be prepared for the tests by KSC personnel. The contractor will also participate in and provide technical guidance during the test and provide an analysis and recommendations after the test. KSC personnel will conduct the test.

Task I. Investigate the neutralization of propellants A-50 and MMH using dry ammonia salts in a Freon 1301 Aerosol. A preliminary effort revealed that nearly complete replacement reaction was obtained between the propellant and the salts.

This task was instituted as a replacement for Task F on June 20, 1968.

Task J. Perform a series of Freon 1301 discharge tests of approximately 5 pounds of Freon heated above its critical temperature, to 160-170° F and 600 psia. The discharge volume should be approximately 120 ft³ and air conditioned to 75° F, 40 percent RH. Discharge time shall be less than one second. Motion picture coverage is required. The object of this task is to obtain a fog-free discharge of Freon 1301 from a superheated condition.

This task was instituted by Amendment Number 2 dated September 13, 1968 to Request Number CC-59100.

APPENDIX II

Hypergolic Ignition Experiments

TABLE AII-1. - Neat N₂O₄ (75 gms) Into A-50/Water

A-50+H ₂ O wt. g	H ₂ O wt. %	O/F wt. ratio	Temperature rise °C	Material Balance	
				Init. Wt. g	Final Wt. g
150	95	10	54	225	154
75	95	20	50	150	86
150	90	5	62	225	154
75	90	10	77	150	78
150	85	3.3	Broke dish and beaker		

TABLE AII-2. - N₂O₄/Water Into Neat A-50 (50 gms)

H ₂ O wt, %	N ₂ O ₄ + H ₂ O wt, g	A-50 wt, g	O/F wt ratio	Temp. rise °C	Material Balance	
					Initial wt g	Final wt g
90	50	50	0.1	52.5	100	90
90	100	50	0.2	55.5	--	--
90	200	50	0.4	61	250	206
90	25	50	0.05	27.5	75	56
90	400	50	0.8	50	450	354
90	300	50	0.6	66	350	237
85	50	50	0.15	75	100	74
85	25	50	0.075	60	75	65
85	100	50	0.30	86.5	150	123
85	200	50	0.60	87	250	151
85	400	50	1.20	80	450	300
75	25	50	0.125	55	75	63
75	50	50	0.25	76	100	82
75	100	50	0.50	98	150	95
75	200	50	1.00	97	250	79
75	400	50	2.00	91	450	190
65	25	50	0.175	76.5	Ignition	
65	25	50	0.175	60.5	75	62
65	50	50	0.35	87	Ignition	

TABLE AII-3. - Neat A-50 Into N₂O₄/Water

N ₂ O ₄ +H ₂ O wt. g	H ₂ O wt. %	O/F wt. ratio	Temperature rise °C	Material Balance	
				Init. Wt. g	Final Wt. g
50	80	0.2	87.5	100	85
100	80	0.4	95	150	124
50	75	0.25	89	100	85
100	75	0.5	91	150	125
50	70	0.3	101.5	100	80
100	70	0.6	102.5	150	121
25	65	0.175	93.5	75	61
50	65	0.35	102	100	75
100	65	0.7	109	150	116
25	60	0.2	101	75	56
50	60	0.4	108.5	100	78
100	60	0.8	111.5	150	112
25	55	0.225	93	Ignited	

TABLE AII-4. - A-50/Water Into Neat N₂O₄ (75 gms)

Fuel/Water Mix		N ₂ O ₄ wt g	O/F ratio	Temp. Rise °C	Material Balance	
% H ₂ O	Total wt g				Initial wt g	Final wt g
95	400	75	3.75	28	475	314
95	200	75	7.5	45	275	190
95	75	75	20	62	150	56
90	400	75	1.88	28	475	313
90	200	75	3.75	32		
90	200	75	3.75	Explosion		

TABLE AII-5. - A-50/Water Into N₂O₄/Water (Equal Dilution)

H ₂ O %	A-50 g	N ₂ O ₄ g	Temperature Rise °C	Material Balance	
				Init., g	Final, g
80	50	50	54	500	460
60	50	50	90	250	213
50	50	50	105	200	153
45	50	50	89	May have ignited	
45	50	50	97	May have ignited	
40	50	50	104	Ignited	
75	100	50	33	600	545
60	100	50	61	375	345
50	100	50	80	300	265
45	100	50	84	273	233
40	60	30	Exploded, broke dish		
40	100	50	Exploded, broke dish		

TABLE AII-6. - Hot A-50/Water Into Cool N₂O₄/Water (Equal Dilution)

H ₂ O %	A-50 g	Mixture Temp., °C	N ₂ O ₄ g	N ₂ O ₄ Temp., °C	Temp. Rise, °C
55	22.5	65	22.5	11	94
50	25	65	25	24	88
50	50	66	50	10	97
45	50	65	50	3	Explosion

TABLE AII-7. - Neat N_2O_4 (75 gms) Into MMH/Water

MMH+H ₂ O wt. g	H ₂ C wt. %	O/F wt. ratio	Temperature rise °C	Material Balance	
				Init. Wt. g	Final Wt. g
150	90	5	40.5	225	154
75	90	10	61.5	150	78
150	85	3.3	40	225	160
75	85	6.7	61	150	75
150	80	2.5	33	225	159
75	80	5	76	150	75
150	75	2	46.5	225	144
75	75	4	Broke dish and beaker		

TABLE AII-8. - N_2O_4 /Water Into Neat MMH (50 gms)

H ₂ O wt, %	N ₂ O ₄ + H ₂ O wt, g	MMH wt, g	O/F wt ratio	Temp. rise °C	Material Balance	
					Initial wt g	Final wt g
85	25	50	0.075	56.5	75	69
85	50	50	0.15	79.8	160	90
85	100	50	0.30	81.5	150	130
85	200	50	0.60	81.5	250	184
85	400	50	1.2	77.0	450	266
65	25	50	0.175	69.5	75	67
65	50	50	0.35	93	100	87
65	100	50	0.7	101	150	113
65	200	50	1.4	89.5	250	157
65	400	50	2.8	78.5	450	151
55	25	50	0.2225	90.5	Ignition	

TABLE AII-9. - Neat MMH (50 gms) Into N_2O_4 /Water

$N_2O_4+H_2O$ wt. g	H_2O wt. %	O/F wt. ratio	Temperature rise $^{\circ}C$	Material Balance	
				Init. Wt. g	Final Wt. g
50	70	0.3	104	100	88
100	70	0.6	85	150	131
50	65	0.35	105	100	88
100	65	0.7	109.5	150	126
50	60	0.4	111.5	100	73
100	60	0.8	110	150	113
25	55	0.225	112	Ignited	

TABLE AII-10. - MMH/Water Into Neat N_2O_4 (75 gms)

Fuel/Water Mix		N_2O_4 wt g	O/F ratio	Temp. Rise $^{\circ}C$	Material Balance	
% H_2O	Total wt g				Initial wt g	Final wt g
95	400	75	3.75	12	475	302
95	200	75	7.5	26	275	142
95	100	75	15	34	175	95
95	75	75	20	43	150	83
90	400	75	1.88	18	--	--
90	200	75	3.75	42	275	195
90	100	75	7.5	51	175	90
90	100	75	7.5	55	175	86
90	75	75	10	63	150	70
80	400	75	0.94	18	475	251
80	200	75	1.88	Explosion		

TABLE AII-11. - MMH/Water Into N₂O₄/Water (Equal Dilution)

H ₂ O %	MMH g	N ₂ O ₄ g	Temperature Rise °C	Material Balance	
				Init., g	Final, g
80	50	50	34	500	470
60	50	50	66	250	235
50	50	50	96	200	170
45	50	50	88	180	146
40	50	50	87	183	153
40	50	50	100	Ignited	
40	50	50	88	Ignited	
75	100	50	40	600	560
60	100	50	55	375	353
50	100	50	64	300	265
45	100	50	76	273	237
40	100	50	68	250	202
40	100	50	75	250	203
35	100	50	--	Ignited	

APPENDIX III

Evaporation of N_2O_4

1. Some Available Information on N_2O_4 Evaporation

The evaporation of N_2O_4 is not listed as a problem in Appendix I, however it does have interest in this program and some reported data provide guidelines to our study of the evaporation of A-50 and MMH from pools. Henderson^{1/} describes 17 experiments in which approximately 100 pounds N_2O_4 was spilled into a 4 ft x 4 ft x 1/4 in. thick stainless steel tray with 8-in. sidewalls. Measurements were made in each test of:

- (1) Elapsed time from spill;
- (2) Propellant weight, therefrom cumulative weight loss, and evaporation rate;
- (3) Pan temperature;
- (4) Propellant temperature;
- (5) Wind speed;
- (6) Relative humidity;
- (7) Air temperature, and temperature gradient from 10 ft to 50 ft above ground.

This work was conducted over a period of time covering the four seasons of the year with widely varying ambient temperatures, humidities, and wind velocities. We could not hope to improve on the experimentation in the time available to us but have attempted to extend the interpretation of data.

Excluding four tests in which the spill tray had been filled with 2 inches of sand, two tests in which it had been filled with 2 inches of concrete, and one test in which only 50 pounds of propellant was spilled, the overall evaporation rates are as given in Table 1. Comparing the first five tests at about 70° F with the second group at about 40° F, one finds surprisingly little effect of air temperature on evaporation rate. Likewise, wind speed is of no overriding importance except as shown in test #3 which was conducted in a very strong wind; humidity was not sufficiently variable to have a demonstrable effect. Therefore we have taken a more detailed look at one specific test (#6) for which the data necessary for constructing a heat balance are given in Table 2. The weight loss of propellant, column 2, gives the required heat input for vaporization, Δq_v , of column 3. Part of this comes from the change of heat content of the propellant, Δq_1 , as it cools from initial temperature, 74° F at the top of column 4, to a minimum temperature of 18° F; another

^{1/} McNerney, John L., David E. Towson, and W. Paul Henderson. "Nitrogen Tetroxide Evaporation Rate Studies," Edgewood Arsenal TM 211-1, August 1966.

TABLE AIII-1.- Evaporation Rates of N₂O₄ as
Reproduced from Reference 1

Test No.	Air temperature,* °F	Wind speed,* mph	Relative humidity,* %	Average evaporation rate, lb/ft ² min	
				First 20 min	First 120 Min
15	75	12	48	0.100	0.046
8	74	8	57	.084	.040
7	70	8	63	.063	.054
5	69	5	43	.066	.041
6	64	12	45	.063	.047
3	46	28	87	0.125	0.083**
2	45	6	53	.094	.036
13	40	17	37	.060	.026
4	36	19	44	.063	.038
1	30	17	42	.056	.031

*Averaged values from readings taken at 5-minute intervals.

**Test completed in 75 minutes.

fraction of the required heat Δq_p is obtained from the heavy (500 lb) steel tray which also cools as shown in column 6. Neglecting other heat inputs, the heat required by convection from the air stream, Δq_c , is given by

$$\Delta q_c = \Delta q_v + \Delta q_l + \Delta q_p. \quad (1)$$

This is given by addition of columns 3, 5, and 7 in column 8. One observes that the propellant reaches minimum temperature in about 20 minutes and that most of the required heat input during this interval is provided by the warm tray and warm propellant. This accounts for the observation (Table 1) that initial vaporization rates are very insensitive to environmental factors.

According to Henderson^{1/}, freezing was visible at about 10 minutes when the recorded temperature was 32° F. Freezing adds heat to the remaining liquid and subsequent melting removes it so the weight loss vs time curve is understandably erratic.

If heat input from the wind stream is assumed to be that given^{2/} for convective flow to a flat plate,

$$\frac{\Delta q}{\Delta t} \text{ (watts)} = 0.0019 A p v (T_a - T_f)/T_a \quad (2)$$

^{2/} International Critical Tables, Volume V, p. 234.

TABLE AIII-2. -Evaporation of N_2O_4 as Function of Time in
Test #6, Reference 1

1	2	3	4	5	6	7	8	9
Time (min)	Weight loss (lb)	Δq_v (kcal)	N_2O_4 temp	Δq_1 (kcal)	tray temp	Δq_p (kcal)	Δq_c (kcal)	Eq (2) (kcal)
0	0	0	74° F	--	72° F	--	0	--
5	8	338	35	-355	55	-130	-147	39
10	15	634	32	-354	44	-215	65	119
15	18	762	20	-438	38	-260	64	215
20	20	845	18	-443	37	-268	134	325
25	25	1055	18	-416	36	-276	363	437
30	30	1270	19	-381	35	-284	605	548
35	35	1480	20	-348	38	-260	872	657
40	36	1520	22	-330	34	-292	898	762
45	37	1565	22	-325	36	-276	964	864
50	38	1605	24	-307	36	-276	1022	966
55	40	1690	26	-285	39	-253	1152	1064
60	41	1735	28	-269	39	-253	1213	1158
75	58	2450	33	-170	40	-245	2035	1416
90	75	3170	40	- 84	42	-230	2856	1638
105	76	3200	41	- 79	39	-253	2868	1836
120	90	3800	51	- 23	35	-284	3493	2004

where A is the tray's surface area, 1500 cm^2 , p is one atmosphere, v is wind velocity in cm/sec , T_a is air temperature, and T_l is liquid temperature ($^{\circ}\text{C}$), a fairly steady input is obtained as given in column 9. This accounts for the total evaporation through 60 minutes (compare 1213 kcal of column 8 with 1158 kcal in column 9). However, it cannot account for the increasing evaporation rate after 60 minutes or for the increasing N_2O_4 temperature. We assume that moisture from the atmosphere is dissolving in this propellant. This was also a particularly troublesome feature of A-50 tests.

